



# ***STIC Search Report***

**EIC 1700**

**STIC Database Tracking Number: 176451**

**TO: Ben Sackey**  
**Location: REM 5B31**  
**Art Unit : 1626**  
**January 20, 2006**

**Case Serial Number: 10/736387**

**From: Kathleen Fuller**  
**Location: EIC 1700**  
**REMSEN 4B28**  
**Phone: 571/272-2505**  
**Kathleen.Fuller@uspto.gov**

## **Search Notes**

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ACCESS DB # 176451  
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Scientific and Technical Information Center

# SEARCH REQUEST FORM

Requester's Full Name: BEN SACKY Examiner #: 73489 Date: 1/11/06  
 Art Unit: 1626 Phone Number: 2-0704 Serial Number: 10/736,357  
 Location (Bldg & room): EN 533 Mailbox #: \_\_\_\_\_ Results Format Preferred (circle) PAPER DISK

To ensure an efficient and quality search, please attach a copy of the cover sheet, claims, and abstract or fill out the following:

Title of Invention: Process for recovering acrylonitrile or methacrylonitrile  
 Inventors (please provide full names): Gochhole et al.

SCIENTIFIC REFERENCE BR  
Sci & Tech Inf. Ctr.

Earliest Priority Date: 01/03/03

JAN 12 RECJ

Search Topic:  
 Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected class, subclasses, keywords, synonyms, acronyms, and registry numbers, and combine with the concept of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc., if known.

\*For Sequence Searches Only: Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.

A process for preparing acrylonitrile & methacrylonitrile comprising contacting a gaseous effluent comprising nitrile monomer with an aqueous gaseous liquid in a first column, contacting the gaseous effluent from 1<sup>st</sup> column with H<sub>2</sub>O in a 2<sup>nd</sup> column, forming a salt of nitrile and co-products, subjecting salt to H<sub>2</sub>O extractive distillation in a recovery distillation column employing H<sub>2</sub>O and collecting nitrile monomer and H<sub>2</sub>O in an overhead decanter, then adding alkaline compd. eg. ammonium carbonate or bicarbonate or carbamate, alkaline diamines and mixtures thereof.

## STAFF USE ONLY

Searcher: K. Fuller

## Type of Search

\_\_\_\_ NA Sequence (#)

\_\_\_\_ AA Sequence (#)

\_\_\_\_ 2-Structure (#)

\_\_\_\_ Bibliographic

Date Completed: 1/30/06

Searcher Prep or Review Time: 40

Online Time: 40

## Vendors and cost where applicable

☒ STN ☐ Dialog

☐ Questel/Orbit ☐ Lexis/Nexis

☐ Westlaw ☐ WWW/Internet

☐ In-house sequence systems

☐ Commercial ☐ Oligomer ☐ Source Length

☐ Interference ☐ SPDI ☐ Encode/Transl

☐ Other (specify): \_\_\_\_\_



# STIC Search Results Feedback Form

**EIC17000**

Questions about the scope or the results of the search? Contact the EIC searcher or contact:

Kathleen Fuller, EIC 1700 Team Leader  
571/272-2505 REMSEN 4B28

## Voluntary Results Feedback Form

- I am an examiner in Workgroup:  Example: 1713
- Relevant prior art found, search results used as follows:

- ☐ 102 rejection
- ☐ 103 rejection
- ☐ Cited as being of interest.
- ☐ Helped examiner better understand the invention.
- ☐ Helped examiner better understand the state of the art in their technology.

Types of relevant prior art found:

- ☐ Foreign Patent(s)
- ☐ Non-Patent Literature  
(journal articles, conference proceedings, new product announcements etc.)

➤ Relevant prior art *not* found:

- ☐ Results verified the lack of relevant prior art (helped determine patentability).
- ☐ Results were not useful in determining patentability or understanding the invention.

Comments:

=> file reg

FILE 'REGISTRY' ENTERED AT 11:31:36 ON 20 JAN 2006

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Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 18 JAN 2006 HIGHEST RN 872163-75-2

DICTIONARY FILE UPDATES: 18 JAN 2006 HIGHEST RN 872163-75-2

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH JULY 14, 2005

Please note that search-term pricing does apply when conducting SmartSELECT searches.

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\*  
\* The CA roles and document type information have been removed from \*  
\* the IDE default display format and the ED field has been added, \*  
\* effective March 20, 2005. A new display format, IDERL, is now \*  
\* available and contains the CA role and document type information. \*  
\*  
\*\*\*\*\*

Structure search iteration limits have been increased. See HELP SLIMITS for details.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

<http://www.cas.org/ONLINE/UG/regprops.html>

=> file hcaplu

FILE 'HCAPLUS' ENTERED AT 11:31:41 ON 20 JAN 2006

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FILE COVERS 1907 - 20 Jan 2006 VOL 144 ISS 5

FILE LAST UPDATED: 19 Jan 2006 (20060119/ED)

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This file contains CAS Registry Numbers for easy and accurate substance identification.

=> d que

L2 10 SEA FILE=REGISTRY ABB=ON (1066-33-7/BI OR 107-13-1/BI OR  
107-15-3/BI OR 110-18-9/BI OR 1111-78-0/BI OR 124-38-9/BI OR  
126-98-7/BI OR 506-87-6/BI OR 7664-41-7/BI OR 7732-18-5/BI)  
L4 1 SEA FILE=REGISTRY ABB=ON 126-98-7  
L5 3 SEA FILE=REGISTRY ABB=ON L2 AND AMMONIUM  
L6 1 SEA FILE=REGISTRY ABB=ON L2 AND CARBAM?  
L7 2 SEA FILE=REGISTRY ABB=ON L2 AND DIAMINE  
L9 2768 SEA FILE=HCAPLUS ABB=ON L4  
L13 38977 SEA FILE=HCAPLUS ABB=ON L5 OR L6 OR L7  
L15 1 SEA FILE=REGISTRY ABB=ON 107-13-1  
L16 28444 SEA FILE=HCAPLUS ABB=ON L15  
L17 122 SEA FILE=HCAPLUS ABB=ON (L16 OR L9) (L) PUR/RL  
L18 76 SEA FILE=HCAPLUS ABB=ON L17 AND (H2O OR AQUEOUS? OR WATER?)  
L19 40 SEA FILE=HCAPLUS ABB=ON L18 AND COLUMN?  
L20 1 SEA FILE=HCAPLUS ABB=ON L19 AND L13  
L21 2 SEA FILE=HCAPLUS ABB=ON L19 AND ALKALIN?  
L22 283 SEA FILE=HCAPLUS ABB=ON (L16 OR L9) AND EXTRACT? AND DISTILL?  
  
L23 238 SEA FILE=HCAPLUS ABB=ON L22 AND (H2O OR AQUEOUS? OR WATER?)  
L24 47 SEA FILE=HCAPLUS ABB=ON L23 AND ALKALI?  
L25 4 SEA FILE=HCAPLUS ABB=ON L23 AND L13  
L26 7 SEA FILE=HCAPLUS ABB=ON L24 AND GAS?  
L27 4 SEA FILE=HCAPLUS ABB=ON L24 AND VAPOR?  
L28 4174 SEA FILE=HCAPLUS ABB=ON (L16 OR L9) (L) PREP/RL  
L29 58 SEA FILE=HCAPLUS ABB=ON L22 AND L28  
L30 47 SEA FILE=HCAPLUS ABB=ON L23 AND L29  
L31 3 SEA FILE=HCAPLUS ABB=ON L30 AND DECANT?  
L32 1 SEA FILE=HCAPLUS ABB=ON L30 AND L13  
L33 8 SEA FILE=HCAPLUS ABB=ON L30 AND (ALKALINE OR ALKALI OR BASE#  
OR AMINE#)  
L34 21 SEA FILE=HCAPLUS ABB=ON L20 OR L21 OR (L25 OR L26 OR L27) OR  
L31 OR L32 OR L33  
L35 25 SEA FILE=HCAPLUS ABB=ON L30 AND (GAS? OR VAPOR?)  
L36 40 SEA FILE=HCAPLUS ABB=ON L34 OR L35

=> d l36 bib abs ind hitstr 1-40

L36 ANSWER 1 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 2005:904397 HCAPLUS

DN 143:230362

TI Process for the purification of an ammoxidation-derived olefinically  
unsaturated nitriles using absorption and extractive  
distillation

IN Godbole, Sanjay P.; Kantak, Milind V.; Wahnschafft, Oliver M.

PA USA

SO U.S. Pat. Appl. Publ., 8 pp.

CODEN: USXXCO

DT Patent

LA English

FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 2005187401	A1	20050825	US 2005-31277	20050106
PRAI	US 2004-535414P	P	20040109		

AB A process for the recovery and purification of olefinically unsatd. nitriles

(e.g., acrylonitrile) from a process stream produced by the ammoxidn. of a hydrocarbon feedstock comprises: contacting the process stream comprising the unsatd. nitrile with an aqueous quench liquid in a quench apparatus to produce a gaseous quench effluent comprising the unsatd. nitrile; contacting the gaseous quench effluent with a liquid comprising water in an absorber apparatus to form an aqueous mixture comprising the absorbed unsatd. nitrile; withdrawing from the absorber apparatus a side-draw stream comprising water and a bottoms stream comprising the unsatd. nitrile; introducing the bottoms stream to a first distillation column where the bottoms stream is distilled in an extractive distillation to form a top fraction comprising the unsatd. nitrile, and directing the side-draw stream comprising water to the upper portion of the first distn. column to assist with the extractive distillation of the unsatd. nitrile in the first distillation column. A process flow diagram is presented.

IC ICM C07C253-34

INCL 558463000

CC 35-2 (Chemistry of Synthetic High Polymers)

Section cross-reference(s): 23, 48

ST unsatd nitrile purifn absorption distn; acrylonitrile purifn absorption distn

IT Columns and Towers

(absorption; in a process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distillation)

IT Monomers

RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process) (acrylic; process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distn.)

IT Distillation columns

(extractive; in a process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distillation)

IT Distillation

(extractive; process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distillation)

IT Cooling

(of an absorber in a process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distillation)

IT Absorption

Ammoxidation

(process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distillation)

IT Nitriles, preparation

RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process) (unsatd.; process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distn.)

IT Coolants

(water; for cooling of an absorber in a process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distillation)

IT 7732-18-5, Water, uses  
 RL: EPR (Engineering process); NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PYP (Physical process); PROC (Process); USES (Uses)  
 (in a process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distn.)

IT 75-05-8, Acetonitrile, processes  
 RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); REM (Removal or disposal); PROC (Process)  
 (in a process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distn.)

IT 107-13-1P, Acrylonitrile, preparation  
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)  
 (process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distillation)

IT 115-07-1, Propene, reactions 7664-41-7, Ammonia, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distillation)

IT 7782-44-7, Oxygen, reactions  
 RL: RGT (Reagent); RACT (Reactant or reagent)  
 (process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distillation)

IT 107-13-1P, Acrylonitrile, preparation  
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)  
 (process for the purification of an ammoxidn.-derived olefinically unsatd. nitriles using absorption and extractive distillation)

RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 2 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN  
 AN 2005:696871 HCAPLUS  
 DN 143:173547  
 TI Process for the purification of olefinically unsaturated nitriles  
 IN Godbole, Sanjay P.; Kantak, Milind V.; Wahnschafft, Oliver M.  
 PA The Standard Oil Company, USA  
 SO PCT Int. Appl., 19 pp.  
 CODEN: PIXXD2  
 DT Patent  
 LA English  
 FAN.CNT 2

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005070880	A1	20050804	WO 2005-US557	20050106
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,				

LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI,  
 NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY,  
 TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW  
 RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,  
 AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,  
 EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT,  
 RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,  
 MR, NE, SN, TD, TG

PRAI US 2004-535414P P 20040109

AB A process for the recovery and purification of olefinically unsatd. nitriles (e.g., acrylonitrile) from a process stream comprises: (a) contacting a process stream comprising an olefinically unsatd. nitrile with an **aqueous** quench liquid in a quench apparatus to produce a **gaseous** quench effluent comprising the olefinically unsatd. nitrile; (b) contacting the **gaseous** quench effluent with a liquid comprising **water** in an absorber apparatus to form an **aqueous** mixture comprising absorbed olefinically unsatd. nitrile; (c) withdrawing from the absorber apparatus a side-draw stream comprising **water** and a stream comprising an olefinically unsatd. nitrile; (d) introducing the stream comprising the olefinically unsatd. nitrile into a first **distillation** column where the stream is **distilled** in an **extractive distillation** to form a fraction comprising an olefinically unsatd. nitrile; and (e) directing the side-draw stream comprising **water** to the first **distillation** column for the **extractive distillation** of the olefinically unsatd. nitrile in the first **distillation** column. A process flow diagram is presented.

IC ICM C07C253-34

ICS C07C255-08

CC 35-2 (Chemistry of Synthetic High Polymers)

Section cross-reference(s): 23, 48

ST olefinically unsatd nitrile **distn** purifn; acrylonitrile **distn** purifn

IT Alkenes, reactions

RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent) (ammoxidn. of)

IT **Distillation**

(**extractive**; in a process for the purification of olefinically unsatd. nitriles)

IT Ammoxidation

**Distillation** columns

(in a process for the purification of olefinically unsatd. nitriles)

IT Nitriles, preparation

RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process) (unsatd.; process for the purification of olefinically unsatd. nitriles)

IT 115-07-1, Propene, reactions

RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent) (ammoxidn. of)

IT 7732-18-5, **Water**, uses

RL: EPR (Engineering process); NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses) (in a process for the purification of olefinically unsatd. nitriles)

IT 107-13-1P, Acrylonitrile, preparation

RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); **PREP (Preparation)**; PROC (Process)

(process for the purification of olefinically unsatd. nitriles)



IT 107-13-1P, Acrylonitrile, preparation  
 RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)  
 (process for the purification of olefinically unsatd. nitriles)  
 RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



RE.CNT 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L36 ANSWER 3 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 2004:606433 HCAPLUS

DN 141:140908

TI Extractive distillation process for recovering acrylonitrile or methacrylonitrile from ammoxidation reaction effluents

IN Godbole, Sanjay P.; Cesa, Mark C.

PA The Standard Oil Company, USA

SO PCT Int. Appl., 12 pp.

CODEN: PIXXD2

DT Patent

LA English

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004063145	A1	20040729	WO 2003-US38691	20031205
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
CA 2516401	AA	20040729	CA 2003-2516401	20031205
EP 1590320	A1	20051102	EP 2003-796689	20031205
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK				
US 2004181086	A1	20040916	US 2003-736387	20031215
PRAI US 2003-437836P	P	20030103		
WO 2003-US38691	W	20031205		

AB A process for the recovery of acrylonitrile or methacrylonitrile from an aqueous solution comprises subjecting the solution to a water extractive distillation by feeding the solution to a distillation column and performing the extractive distillation and using solvent water introduced at the top of the column, removing a first overhead vapor stream of acrylonitrile or methacrylonitrile with some water from the top of the column, and a first liquid stream containing water and impurities from the bottom of the column, the contents of the column maintained at a substantially neutral pH by adding a sufficient amount of at least one alkaline compound selected from ammonium carbonate, ammonium bicarbonate, ammonium carbamate, and alkylene diamines (e.g., TMEDA) to the overhead decanter and/or to the

solvent water.

IC ICM C07C253-26  
ICS C07C253-34; C07C255-08

CC 35-2 (Chemistry of Synthetic High Polymers)  
Section cross-reference(s): 23, 48

ST acrylonitrile monomer recovery **extractive distn**;  
methacrylonitrile monomer recovery **extractive distn**

IT Monomers  
RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)  
(acrylonitrile or methacrylonitrile; **extractive distn**  
. process for recovering acrylonitrile or methacrylonitrile from  
ammoxidn. reaction effluents)

IT Separators  
(decanters; in an **extractive distillation**  
process for recovering acrylonitrile or methacrylonitrile from  
ammoxidn. reaction effluents)

IT Amines, reactions  
RL: RGT (Reagent); RACT (Reactant or reagent)  
(diamines, aliphatic, **bases**; in an **extractive distillation** process for recovering acrylonitrile or  
methacrylonitrile from ammoxidn. reaction effluents)

IT Distillation  
Distillation columns  
(**extractive**; **extractive distillation** process  
for recovering acrylonitrile or methacrylonitrile from ammoxidn.  
reaction effluents)

IT Bases, reactions  
RL: RGT (Reagent); RACT (Reactant or reagent)  
(in an **extractive distillation** process for recovering  
acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

IT 506-87-6P, Ammonium carbonate  
RL: PNU (Preparation, unclassified); RGT (Reagent); PREP (Preparation);  
RACT (Reactant or reagent)  
(**base**; in an **extractive distillation** process  
for recovering acrylonitrile or methacrylonitrile from ammoxidn.  
reaction effluents)

IT 107-15-3, Ethylene diamine, reactions 110-18-9, TMEDA  
1066-33-7, Ammonium bicarbonate 1111-78-0, Ammonium  
carbamate  
RL: RGT (Reagent); RACT (Reactant or reagent)  
(**base**; in an **extractive distillation** process  
for recovering acrylonitrile or methacrylonitrile from ammoxidn.  
reaction effluents)

IT 107-13-1P, Acrylonitrile, preparation 126-98-7P,  
Methacrylonitrile  
RL: PEP (Physical, engineering or chemical process); PUR  
(**Purification or recovery**); PYP (Physical process); PREP  
(**Preparation**); PROC (Process)  
(**extractive distillation** process for recovering  
acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

IT 124-38-9, Carbon dioxide, reactions 7664-41-7, Ammonia, reactions  
RL: RGT (Reagent); RACT (Reactant or reagent)  
(in the in-situ preparation of ammonium carbonate)

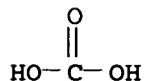
IT 7732-18-5, Water, reactions  
RL: NUU (Other use, unclassified); RGT (Reagent); RACT (Reactant or  
reagent); USES (Uses)  
(solvent; **extractive distillation** process for recovering  
acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

IT 506-87-6P, Ammonium carbonate

RL: PNU (Preparation, unclassified); RGT (Reagent); PREP (Preparation);  
RACT (Reactant or reagent)  
(base; in an extractive distillation process  
for recovering acrylonitrile or methacrylonitrile from ammoxidn.  
reaction effluents)

RN 506-87-6 HCAPLUS

CN Carbonic acid, diammonium salt (8CI, 9CI) (CA INDEX NAME)



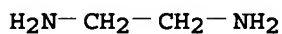
●2 NH<sub>3</sub>

IT 107-15-3, Ethylene diamine, reactions 110-18-9, TMEDA  
1066-33-7, Ammonium bicarbonate 1111-78-0, Ammonium  
carbamate

RL: RGT (Reagent); RACT (Reactant or reagent)  
(base; in an extractive distillation process  
for recovering acrylonitrile or methacrylonitrile from ammoxidn.  
reaction effluents)

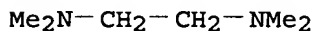
RN 107-15-3 HCAPLUS

CN 1,2-Ethanediamine (9CI) (CA INDEX NAME)



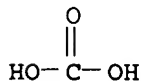
RN 110-18-9 HCAPLUS

CN 1,2-Ethanediamine, N,N,N',N'-tetramethyl- (9CI) (CA INDEX NAME)



RN 1066-33-7 HCAPLUS

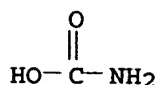
CN Carbonic acid, monoammonium salt (8CI, 9CI) (CA INDEX NAME)



● NH<sub>3</sub>

RN 1111-78-0 HCAPLUS

CN Carbamic acid, monoammonium salt (8CI, 9CI) (CA INDEX NAME)

● NH<sub>3</sub>

IT 107-13-1P, Acrylonitrile, preparation 126-98-7P,  
Methacrylonitrile  
RL: PEP (Physical, engineering or chemical process); PUR  
(Purification or recovery); PYP (Physical process); PREP  
(Preparation); PROC (Process)  
(extractive distillation process for recovering  
acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

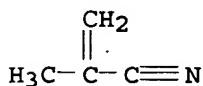
RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



RN 126-98-7 HCAPLUS

CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



L36 ANSWER 4 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 2004:473397 HCAPLUS

DN 141:24127

TI Method for inhibiting polymerization during the recovery and purification  
of unsaturated mononitriles

IN Rosen, Bruce I.; Firth, Bruce E.

PA USA

SO U.S. Pat. Appl. Publ., 12 pp.  
CODEN: USXXCO

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 2004110977	A1	20040610	US 2002-309962	20021204
	US 6984749	B2	20060110		
	CA 2506409	AA	20040624	CA 2003-2506409	20031112
	WO 2004052842	A1	20040624	WO 2003-US36060	20031112
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW				
RW:	BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ,				

BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

EP 1567481 A1 20050831 EP 2003-781907 20031112  
 R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK

BR 2003016857 A 20051018 BR 2003-16857 20031112  
 US 2004249182 A1 20041209 US 2004-852277 20040524

PRAI US 2002-309962 A 20021204  
 WO 2003-US36060 W 20031112

OS MARPAT 141:24127

AB Economical processes for recovery and refining of valuable N-containing organic compds. formed by catalytic oxidation of  $\geq 1$  feed compound selected from propane, propylene, isobutane and isobutylene in the presence of  $\text{NH}_3$  to produce a gaseous effluent containing unsatd. mononitriles are described. Processes include quenching the gaseous reactor effluent with an aqueous quench liquid; forming an aqueous solution comprising the corresponding unsatd. mononitrile, HCN and other organic coproducts; and using an integrated sequence of distns. and phase sepns. to recover for recycle of a useful aqueous liquid, and obtain the desired N-containing products. Aqueous solns. are fractionated in an integrated system of multi-stage columns while introducing an effective polymerization inhibiting amount of  $\geq 1$  member of a preselected class of p-phenylenediamine compds. such as N,N'-di-sec-butyl-p-phenylenediamine.

IC ICM C07C253-26

INCL 558320000

CC 35-2 (Chemistry of Synthetic High Polymers)  
 Section cross-reference(s): 23

ST acrylonitrile recovery polymn inhibiting phenylenediamine

IT **Distillation**  
**Extraction**  
 Phase separation  
 Polymerization inhibitors  
 (phenylenediamine compds. for inhibiting polymerization during the recovery and purification of unsatd. mononitriles)

IT 101-96-2, N,N'-Di-sec-butyl-p-phenylenediamine 4251-01-8,  
 N,N'-Di-sec-propyl-p-phenylenediamine 10368-05-5, N,N'-Diisobutyl-p-phenylenediamine 42574-83-4  
 RL: CAT (Catalyst use); USES (Uses)  
 (phenylenediamine compds. for inhibiting polymerization during the recovery and purification of unsatd. mononitriles)

IT 107-13-1P, Acrylonitrile, preparation 126-98-7P,  
 Methacrylonitrile  
 RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)  
 (phenylenediamine compds. for inhibiting polymerization during the recovery and purification of unsatd. mononitriles)

IT 115-07-1, Propylene, reactions 115-11-7, Isobutylene, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (phenylenediamine compds. for inhibiting polymerization during the recovery and purification of unsatd. mononitriles)

IT 107-13-1P, Acrylonitrile, preparation 126-98-7P,  
 Methacrylonitrile  
 RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)  
 (phenylenediamine compds. for inhibiting polymerization during the recovery and purification of unsatd. mononitriles)

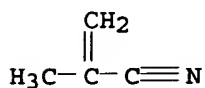
RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



RN 126-98-7 HCAPLUS

CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



RE.CNT 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L36 ANSWER 5 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 2000:337482 HCAPLUS

DN 132:308815

TI Recovery and refining of olefinic nitrile

IN Guan, Xingya; Zhang, Hui; Fang, Yongcheng

PA Sino Petro-Chemical Corp., Peop. Rep. China

SO Faming Zhuanli Shenqing Gongkai Shuomingshu, 12 pp.

CODEN: CNXXEV

DT Patent

LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	CN 1217324	A	19990526	CN 1997-106712	19971113
	CN 1059897	B	20001227		
PRAI	CN 1997-106712		19971113		

AB The process comprises feeding the crude olefinic nitrile gas to the bottom of quenching tower, cooling successively with a water-containing cooling liquid and at pH <7 with the temperature controlled at 70-90° for the lower section, 75-85° for the medium section and 25-45° for the upper section, feeding the condensed liquid to extraction tower, feeding the olefinic nitrile and HCN containing un-condensed liquid to absorption tower, distilling to remove water and impurity, distilling the condensed solution in the presence of acetic acid as stabilizer in HCN distillation tower with the pressure at the top of tower controlled at -0.05 to 0 MPa to obtain olefinic nitrile liquid and HCN gas; and separating the liquid from the side of the tower to obtain organic phase and solution for recycle. The process is preferably used for preparing acrylonitrile. Acrylonitrile is synthesized by ammoxidn. of propene with NH<sub>3</sub> and air at 440° and 0.5 kg/cm<sup>2</sup>. Acrylic acid, cyanic acid and acetonitrile are the byproducts of acrylonitrile synthesis.

IC ICM C07C255-08

ICS C07C253-34

CC 35-2 (Chemistry of Synthetic High Polymers)

ST olefinic nitrile recovery refining acrylonitrile synthesis

IT Ammoxidation

(recovery and refining of olefinic nitrile)

IT Nitriles, preparation

RL: IMF (Industrial manufacture); PREP (Preparation)

(unsatd.; recovery and refining of olefinic nitrile)

IT 107-13-1P, Acrylonitrile, preparation

RL: IMF (Industrial manufacture); PREP (Preparation)  
 (recovery and refining of olefinic nitrile)  
 IT 115-07-1, Propene, reactions 7664-41-7, Ammonia, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (recovery and refining of olefinic nitrile)  
 IT 64-19-7, Acetic acid, uses  
 RL: NUU (Other use, unclassified); USES (Uses)  
 (stabilizer; recovery and refining of olefinic nitrile)  
 IT 107-13-1P, Acrylonitrile, preparation  
 RL: IMF (Industrial manufacture); PREP (Preparation)  
 (recovery and refining of olefinic nitrile)  
 RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 6 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1999:622330 HCAPLUS

DN 131:229159

TI Recovery of organic compounds from the process flare headers of  
 ammoxidation processes

IN Keckler, Kenneth P.; Godbole, Sanjay P.

PA The Standard Oil Company, USA

SO U.S., 4 pp.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 5959134	A	19990928	US 1998-82403	19980520
	CA 2332502	AA	19991125	CA 1999-2332502	19990518
	WO 9959963	A1	19991125	WO 1999-US11030	19990518
	W: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
	RW: GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
	AU 9940866	A1	19991206	AU 1999-40866	19990518
	BR 9910601	A	20010116	BR 1999-10601	19990518
	TR 200003412	T2	20010321	TR 2000-200003412	19990518
	EP 1087936	A1	20010404	EP 1999-924343	19990518
	R: AT, BE, DE, ES, FR, GB, NL				
	JP 2002515479	T2	20020528	JP 2000-549582	19990518
	RU 2258695	C2	20050820	RU 2000-131596	19990518
	TW 584575	B	20040421	TW 1999-88108210	19990608
	BG 104923	A	20010531	BG 2000-104923	20001107
PRAI	US 1998-82403	A	19980520		
	WO 1999-US11030	W	19990518		

AB A process for the enhanced recovery of waste orgs. (e.g., hydrogen cyanide) from the process flare material obtained from the reactor effluent of an ammoxidn. reaction of propylene or isobutylene is described which comprises directing a portion of the process flare header material to an organic recovery process selected from aqueous-phase

countercurrent scrubbing, organic-phase countercurrent scrubbing, aq  
 .-phase co-current scrubbing, organic-phase co-current scrubbing,  
**distillation, extraction**, leaching, adsorption, absorption,  
 selective condensation, and selective reaction.

IC ICM C07C253-00

INCL 558320000

CC 35-2 (Chemistry of Synthetic High Polymers)

Section cross-reference(s): 23, 45, 48, 59

ST hydrogen cyanide recovery ammoxidn process; org compd recovery ammoxidn  
 process waste gas scrubbing

IT Ammoxidation

(recovery of organic compds. from the process flare headers of ammoxidn.  
 processes)

IT Absorption

Adsorption

**Distillation**

**Extraction**

Scrubbing

(recovery of organic compds. from the process flare headers of ammoxidn.  
 processes via)

IT **Distillation** columns

(recovery of organic compds. from the process flare headers of ammoxidn.  
 processes via a contactor in)

IT **126-98-7P, Methacrylonitrile**

RL: IMF (Industrial manufacture); **PREP (Preparation)**

(recovery of organic compds. from the process flare headers of ammoxidn.  
 processes)

IT **107-13-1P, Acrylonitrile, preparation**

RL: IMF (Industrial manufacture); PUR (Purification or recovery);

**PREP (Preparation)**

(recovery of organic compds. from the process flare headers of ammoxidn.  
 processes)

IT 74-90-8P, Prussic acid, preparation

RL: PUR (Purification or recovery); **PREP (Preparation)**

(recovery of organic compds. from the process flare headers of ammoxidn.  
 processes)

IT 115-07-1, Propene, reactions 115-11-7, Isobutene, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(recovery of organic compds. from the process flare headers of ammoxidn.  
 processes)

IT 7732-18-5, **Water**, uses

RL: NUU (Other use, unclassified); **USES (Uses)**

(solvent; recovery of organic compds. from the process flare headers of  
 ammoxidn. processes)

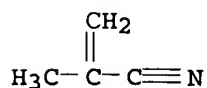
IT **126-98-7P, Methacrylonitrile**

RL: IMF (Industrial manufacture); **PREP (Preparation)**

(recovery of organic compds. from the process flare headers of ammoxidn.  
 processes)

RN 126-98-7 HCAPLUS

CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



IT **107-13-1P, Acrylonitrile, preparation**

RL: IMF (Industrial manufacture); PUR (Purification or recovery);

**PREP (Preparation)**



(recovery of organic compds. from the process flare headers of ammoxidn. processes)

RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



RE.CNT 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L36 ANSWER 7 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1998:787995 HCAPLUS

DN 130:54119

TI **Extractive distillation:** Separating  
close-boiling-point components

AU Lee, Fu-Ming

CS GTC Technology Corp., Houston, TX, 77077, USA

SO Chemical Engineering (New York) (1998), 105(12), 112-116, 118, 120-121  
CODEN: CHEEA3; ISSN: 0009-2460

PB McGraw-Hill Companies, Inc.

DT Journal

LA English

AB **Extractive distillation** has been used in the chemical process  
industries for years, although not as widely as traditional **distn**  
. and azeotropic **distillation**. The selection of cosolvents using  
polarity (e.g., dielec. constant) as an initial guideline is discussed for  
various hydrocarbon sepns. using **extractive distillation**

CC 48-1 (Unit Operations and Processes)

Section cross-reference(s): 51

ST **extractive distn** close boiling point component

IT Solvents

(cosolvents; **extractive distillation** for separation of close  
b.p. components)

IT Dielectric constant

Polarity

(extractive **distillation** for separation of close b.p.  
components)

IT Hydrocarbons, processes

Natural gas condensates

RL: PEP (Physical, engineering or chemical process); PUR (Purification or  
recovery); PREP (Preparation); PROC (Process)(extractive **distillation** for separation of close b.p.  
components)IT **Distillation**(extractive; **extractive distillation** for separation  
of close b.p. components)

IT Solvents

(mixts.; MIST; **extractive distillation** for separation of close  
b.p. components)

IT Volatility

(relative; **extractive distillation** for separation of close  
b.p. components)

IT 108-08-7P, 2,4-Dimethylpentane 108-88-3P, Toluene, processes

110-82-7P, Cyclohexane, processes 142-82-5P, n-Heptane, processes

464-06-2P, 2,2,3-Trimethylbutane 562-49-2P, 3,3-Dimethylpentane

565-59-3P, 2,3-Dimethylpentane 589-34-4P, 3-Methylhexane 590-35-2P,

2,2-Dimethylpentane 591-76-4P, 2-Methylhexane 28729-52-4P,

Dimethylcyclopentane

RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PREP (Preparation); PROC (Process)

(extractive distillation for separation of close b.p. components)

IT 56-81-5, Glycerol, properties 57-55-6, 1,2-Propanediol, properties 62-53-3, Aniline, properties 64-17-5, Ethanol, properties 67-56-1, Methanol, properties 67-71-0, Dimethylsulfone 71-23-8, 1-Propanol, properties 71-36-3, 1-Butanol, properties 75-05-8, Acetonitrile, properties 75-12-7, Formamide, properties 75-50-3, Trimethylamine, properties 75-52-5, Nitromethane, properties 78-81-9, Iso-Butylamine 78-83-1, 2-Methyl-1-propanol, properties 78-92-2, 2-Butanol 87-99-0, Xylitol 95-48-7, o-Cresol, properties 95-65-8, 3,4-Dimethylphenol 96-41-3, Cyclopentanol 96-49-1, Ethylene carbonate 100-41-4, Ethylbenzene, properties 100-47-0, Benzonitrile, properties 103-69-5, n-Ethylaniline 107-12-0, Propionitrile 107-13-1, Acrylonitrile, properties 107-15-3, Ethylene diamine, properties 107-21-1, Ethylene glycol, properties 107-87-9, 2-Pentanone 108-39-4, properties 108-93-0, Cyclohexanol, properties 108-95-2, Phenol, properties 109-06-8, 2-Methyl pyridine 109-86-4, 2-Methoxyethanol 109-99-9, Tetrahydrofuran, properties 110-59-8, Pentanenitrile 110-63-4, 1,4-Butanediol, properties 110-80-5, 2-Ethoxyethanol 110-91-8, Morpholine, properties 110-96-3, Diisobutylamine 111-13-7, 2-Octanone 111-27-3, 1-Hexanol, properties 111-70-6, 1-Heptanol 111-87-5, 1-Octanol, properties 111-92-2, Dibutylamine 112-27-6, Triethylene glycol 112-30-1, 1-Decanol 112-53-8, 1-Dodecanol 112-72-1, 1-Tetradecanol 121-69-7, N,N-Dimethylaniline, properties 123-39-7, N-Methylformamide 123-91-1, 1,4-Dioxane, properties 123-96-6, 2-Octanol 124-40-3, Dimethylamine, properties 126-33-0, Sulfolane 127-19-5, N,N-Dimethylacetamide 137-32-6, 2-Methyl-1-butanol 142-68-7, Tetrahydropyran 504-63-2, 1,3-Propanediol 543-49-7, 2-Heptanol 589-55-9, 4-Heptanol 589-82-2, 3-Heptanol 591-78-6, 2-Hexanone 598-03-8, Di-n-propyl sulfone 680-31-9, Tris(dimethylamino)phosphine oxide, properties 872-50-4, N-Methyl pyrrolidone, properties 872-93-5, 3-Methylsulfolane 6032-29-7, 2-Pentanol 7443-70-1, cis-2-Methylcyclohexanol 7732-18-5, Water, properties 18720-62-2, 2-Methyl-3-heptanol

RL: PRP (Properties)

(extractive distillation for separation of close b.p. components)

IT 107-13-1, Acrylonitrile, properties 107-15-3, Ethylene diamine, properties

RL: PRP (Properties)

(extractive distillation for separation of close b.p. components)

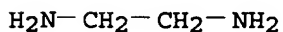
RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



RN 107-15-3 HCAPLUS

CN 1,2-Ethanediamine (9CI) (CA INDEX NAME)



RE.CNT 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L36 ANSWER 8 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1989:58282 HCAPLUS

DN 110:58282

TI Process for recovery of acrylonitrile and lactonitrile from acrylonitrile synthesis mixture residues by **extraction** with salt solutions

IN Schnurpfeil, Dieter; Parthey, Manfred; Wiegner, Jens Peter

PA VEB Chemische Werk, Ger. Dem. Rep.

SO Ger. (East), 3 pp.

CODEN: GEXXA8

DT Patent

LA German

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DD 257066	A1	19880601	DD 1987-299256	19870115
PRAI	DD 1987-299256		19870115		

AB Lactonitrile and acrylonitrile are recovered from nitrile-containing organic solns. (containing 35-55% lactonitrile and 15-25% acrylonitrile) obtained from **distillation** residues prepared during acrylonitrile synthesis from C<sub>2</sub>H<sub>2</sub> and HCN, by **extraction** with **aqueous** salts solns. and subsequent **back extraction** Solns. containing 20-30% alkali metal halides and/or alkaline earth metal halides are used with an **extraction** solution-**distillation** residue ratio of 2-5:1. This process facilitates waste stream processing and overcomes potential ecol. problems. Thus, a **distillation** residue (100 mL), containing acetaldehyde 8, acrylonitrile 15, cyanobutadiene 3, chlorocyclobutadiene 11, lactonitrile 48, and **water** 15, was **extracted** with 200 mL of 25% **aqueous** BaCl<sub>2</sub> solution, producing an organic phase containing chlorocyanobutenes 75, cyanobutadienes 15, lactonitrile 6, acrylonitrile 4, and **water** 2%. This **aqueous** phase was **back extracted** 3 times with 100-mL portions of CH<sub>2</sub>Cl<sub>2</sub>, and the solvent evaporated, producing an **extract** consisting of lactonitrile 70, acrylonitrile 20, and **water** 10%.

IC ICM C07C121-34

ICS C07C121-32; C07C120-02

CC 35-2 (Chemistry of Synthetic High Polymers)

Section cross-reference(s): 23

ST lactonitrile acrylonitrile **distn** residue recovery; barium chloride **extn** lactonitrile recovery; alk earth halide **extn** acrylonitrile; alkali metal halide **extn** acrylonitrile

IT Alkali metal halides, uses and miscellaneous

Alkaline earth halides

RL: USES (Uses)

(solns., **extraction** of acrylonitrile and lactonitrile by, from acrylonitrile-synthesis **distillation** residues)

IT 107-13-1P, Acrylonitrile, preparation

RL: PREP (Preparation)

(**extraction** of lactonitrile and, from acrylonitrile-manufacture **distillation** residues, with **alkaline** earth-and/or **alkali** metal halide solns.)

IT 78-97-7P, Lactonitrile

RL: PREP (Preparation)

(recovery of acrylonitrile and, from acrylonitrile-manufacture **distn** . residues, by **extraction** with **alkaline** earth-and/or **alkali** metal halides)

IT 7647-14-5, Sodium chloride, uses and miscellaneous 10361-37-2, Barium chloride, uses and miscellaneous

RL: USES (Uses)

(solns., **extraction** of acrylonitrile and lactonitrile with, from

acrylonitrile-synthesis distillation residues)  
 IT 107-13-1P, Acrylonitrile, preparation  
 RL: PREP (Preparation)  
 (extraction of lactonitrile and, from acrylonitrile-manufacture  
 distillation residues, with alkaline earth-and/or  
 alkali metal halide solns.)  
 RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 9 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1988:551906 HCAPLUS

DN 109:151906

TI Simultaneous removal of products and byproducts from gases from  
 the ammoxidation of hydrocarbons

IN Schymalla, Alfred; Martin, Andreas; French, Juergen; Mueller, Guenter;  
 Luecke, Bernhard; Seeboth, Helmuth; Herbig, Herbert; Krause, Bernd

PA Akademie der Wissenschaften der DDR, Ger. Dem. Rep.

SO Ger. (East), 5 pp.

CODEN: GEXXA8

DT Patent

LA German

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DD 251876	A3	19871202	DD 1982-239747	19820511
PRAI	DD 1982-239747		19820511		

OS CASREACT 109:151906

AB Nitriles prepared by ammoxidn. of alkyl-substituted hydrocarbons (e.g.,  
 acrylonitrile and 4-methoxybenzonitrile) are separated from the reaction  
 gases by scrubbing with an emulsion of mutually immiscible  
 solvents (e.g., PhMe and aqueous NaOH, or PhMe and H<sub>2</sub>O).  
 In the continuous countercurrent scrubbing process, the emulsion breaks  
 once it leaves the turbulent mixing environment and allows each product or  
 byproduct to be removed from the solvent by extraction or  
 distillation

IC ICM B01D053-14

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

Section cross-reference(s): 48

ST nitrile manuf ammoxidn hydrocarbon; countercurrent scrubbing ammoxidn  
 reaction mixt

IT Hydrocarbons, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (ammoxidn. of, nitriles from)

IT Nitriles, preparation

RL: PREP (Preparation)  
 (manufacture of, by hydrocarbon ammoxidn.)

IT Ammoxidation

(of hydrocarbons, nitrile manufacture by)

IT 115-07-1, Propylene, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (ammoxidn. of, acrylonitrile from)

IT 104-93-8, 4-Methoxytoluene

RL: PROC (Process)  
 (ammoxidn. of, methoxybenzonitrile from)

IT 7664-41-7, Ammonia, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (ammoxidn. with, of hydrocarbons, nitriles from)

IT 874-90-8P, 4-Methoxybenzonitrile  
 RL: PREP (Preparation)  
 (manufacture of, by ammoxidn. of methoxytoluene)

IT 107-13-1P, Acrylonitrile, preparation  
 RL: PREP (Preparation)  
 (manufacture of, by propylene ammoxidn.)

IT 1310-73-2, Sodium hydroxide, uses and miscellaneous  
 RL: USES (Uses)  
 (solvents, with toluene, for nitrile removal from ammoxidn. reaction mixts.)

IT 108-88-3, Toluene, uses and miscellaneous  
 RL: USES (Uses)  
 (solvents, with water or sodium hydroxide, for removal of nitriles from ammoxidn. reaction mixts.)

IT 107-13-1P, Acrylonitrile, preparation  
 RL: PREP (Preparation)  
 (manufacture of, by propylene ammoxidn.)

RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 10 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1987:33593 HCAPLUS

DN 106:33593

TI Energy-efficient process for recovery of unsaturated nitriles

IN Katsuta, Kazumasa

PA Asahi Chemical Industry Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 3 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
PI	JP 61180757	A2	19860813	JP 1985-20597	19850205
PRAI	JP 1985-20597		19850205		

AB In the recovery of unsatd. nitriles (e.g., methacrylonitrile) by the **extraction distillation** of the unsatd. nitrile-containing ammoxidn. mixts. absorbed in water, the **extraction distillation** mixture was discharged as a side cut which was then phase-separated in a **decanter**, and the oil layer was fed to the recovery tower for removal of HCN and water and the aqueous layer was recycled to the **extraction distillation** tower.

IC ICM C07C121-32

ICS C07C120-00

CC 35-2 (Chemistry of Synthetic High Polymers)

Section cross-reference(s): 23

ST methacrylonitrile recovery energy efficiency; ammoxidn isobutene

methacrylonitrile recovery

IT Ammoxidation

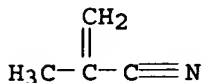
(of isobutene, methacrylonitrile recovery in)

IT Energy

(saving of, in recovery of methacrylonitrile)

IT 115-11-7, Isobutene, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (ammoxidn. of, methacrylonitrile recovery in)  
 IT 126-98-7P, Methacrylonitrile  
 RL: PREP (Preparation)  
 (recovery of, from ammoxidn. mixture of isobutene)  
 IT 126-98-7P, Methacrylonitrile  
 RL: PREP (Preparation)  
 (recovery of, from ammoxidn. mixture of isobutene)  
 RN 126-98-7 HCAPLUS  
 CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



L36 ANSWER 11 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1984:511541 HCAPLUS

DN 101:111541

TI Methacrylonitrile recovery

PA Asahi Chemical Industry Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 3 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 59053454	A2	19840328	JP 1982-164288	19820921
	JP 61033810	B4	19860804		
PRAI	JP 1982-164288		19820921		

AB Hot propylene ammoxidn. gas containing 4.8% methacrylonitrile [126-98-7] was cooled from 200° to 36° in a cooling tower by contact with circulating cold H<sub>2</sub>O to give 2 layers at the bottom. The organic layer was separated and bypassed to extractive distillation, while the aqueous layer was cooled and recycled to the top, thus reducing the load of the absorption step. A higher temperature, e.g. 42°, gave a homogeneous bottom mixture

IC C07C121-32; C07C120-00

CC 35-2 (Chemistry of Synthetic High Polymers)

Section cross-reference(s): 45

ST methacrylonitrile recovery water absorption; distn

methacrylonitrile ammoxidn gas

IT Distillation apparatus

(for separating methacrylonitrile from propylene ammoxidn. gas)

IT 126-98-7P

RL: PREP (Preparation)

(recovery of, from propylene ammoxidn. gas, by cold water absorption and extractive distillation)

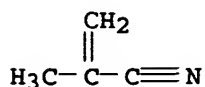
IT 126-98-7P

RL: PREP (Preparation)

(recovery of, from propylene ammoxidn. gas, by cold water absorption and extractive distillation)

RN 126-98-7 HCAPLUS

CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



L36 ANSWER 12 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1984:511540 HCAPLUS

DN 101:111540

TI Methacrylonitrile recovery

PA Asahi Chemical Industry Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 3 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 59053452	A2	19840328	JP 1982-164286	19820921
	JP 61058468	B4	19861211		
PRAI	JP 1982-164286		19820921		

AB The methacrylonitrile (I) [126-98-7] in propylene ammoxidn. gas was absorbed with a min. amount of cold H<sub>2</sub>O to give a 2-layer bottom mixture, e.g. an aqueous layer containing 2.9% I and an organic layer containing 87% I. Each layer was sep. fed to a 68-plate column for extractive distillation, e.g. at the 42nd and 32nd plate, resp. This improved the energy balance.

IC C07C121-32; C07C120-00

CC 35-2 (Chemistry of Synthetic High Polymers)

Section cross-reference(s): 45

ST ammoxidn gas methacrylonitrile recovery; cold water absorption methacrylonitrile

IT 126-98-7P

RL: PREP (Preparation)

(recovery of, from propylene ammoxidn. gas, by cold water absorption)

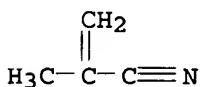
IT 126-98-7P

RL: PREP (Preparation)

(recovery of, from propylene ammoxidn. gas, by cold water absorption)

RN 126-98-7 HCAPLUS

CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



L36 ANSWER 13 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1984:511538 HCAPLUS

DN 101:111538

TI Methacrylonitrile purification

PA Asahi Chemical Industry Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 4 pp.

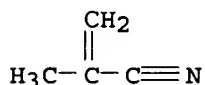
CODEN: JKXXAF

DT Patent

LA Japanese

## FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 59053453	A2	19840328	JP 1982-164287	19820921
PRAI	JP 1982-164287		19820921		
AB	The bottom fraction of a <b>distillation</b> column containing 90% methacrylonitrile (I) [126-98-7] and 10% isobutyronitrile (II) [78-82-0] was recycled to a circulating cooling water tower for hot ammoxidn. gas, and the II contaminant was removed by <b>extractive distillation</b> . The recycling minimized loss of I.				
IC	C07C121-32; C07C120-00				
CC	35-2 (Chemistry of Synthetic High Polymers) Section cross-reference(s): 45				
ST	methacrylonitrile purifn <b>distn</b> ; isobutyronitrile removal methacrylonitrile <b>distn</b>				
IT	<b>Distillation</b> apparatus (for removal of isobutyronitrile from methacrylonitrile)				
IT	<b>126-98-7P</b> RL: PUR (Purification or recovery); PREP (Preparation) (purification of, by <b>extractive distillation</b> , for removal of isobutyronitrile)				
IT	78-82-0 RL: REM (Removal or disposal); PROC (Process) (removal of, from methacrylonitrile, by <b>extractive distillation</b> )				
IT	<b>126-98-7P</b> RL: PUR (Purification or recovery); PREP (Preparation) (purification of, by <b>extractive distillation</b> , for removal of isobutyronitrile)				
RN	126-98-7 HCAPLUS				
CN	2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)				



L36 ANSWER 14 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1983:423085 HCAPLUS

DN 99:23085

TI Recovery and purification of olefinic nitriles

IN Wu, Hsin C.

PA Standard Oil Co., USA

SO U.S., 6 pp. Cont.-in-part of U.S. Ser. No. 446,557, abandoned.

CODEN: USXXAM

DT Patent

LA English

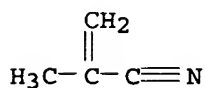
## FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 4377444	A	19830322	US 1975-535402	19750113
PRAI	US 1970-29022	A2	19700416		
	US 1971-185721	A1	19711001		
	US 1974-446557	A2	19740227		
AB	Olefinic nitriles are recovered from olefin ammoxidn. product streams containing olefinic nitriles, HCN, MeCN, and carbonyl compds. by feeding the mixture to an <b>extractive distillation</b> column with several fractionating trays at a point above the middle of the column, feeding				



water as the extraction solvent at 60-120°F, removing a vapor sidestream at a point below the middle of the column, and stripping HCN, MeCN, and carbonyl compds. from the sidestream. Thus, crude methacrylonitrile (I) [126-98-7] from ammoxidn. of isobutylene [115-11-7] was refined to 99.645% purity, yielding a product containing less carbonyl compds. than conventionally purifd. I.

IC B01D003-34  
 INCL 203096000  
 CC 35-2 (Chemistry of Synthetic High Polymers)  
 ST methacrylonitrile purifn; olefin ammoxidn nitrile purifn; isobutylene ammoxidn methacrylonitrile; extractive distn sidestream stripping  
 IT Ammoxidation  
 (of olefins, purification of olefinic nitriles manufactured by)  
 IT Distillation  
 (extractive, with vapor sidestream stripping and recycling, for purification of crude olefinic nitriles)  
 IT 115-07-1, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (ammoxidn. of, purification of acrylonitrile manufactured by)  
 IT 115-11-7, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (ammoxidn. of, purification of methacrylonitrile manufactured by)  
 IT 126-98-7P  
 RL: PUR (Purification or recovery); PREP (Preparation)  
 (purification of, from isobutylene ammoxidn. product mixts.)  
 IT 107-13-1P, preparation  
 RL: PUR (Purification or recovery); PREP (Preparation)  
 (purification of, from propylene ammoxidn. product mixts.)  
 IT 126-98-7P  
 RL: PUR (Purification or recovery); PREP (Preparation)  
 (purification of, from isobutylene ammoxidn. product mixts.)  
 RN 126-98-7 HCAPLUS  
 CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



IT 107-13-1P, preparation  
 RL: PUR (Purification or recovery); PREP (Preparation)  
 (purification of, from propylene ammoxidn. product mixts.)  
 RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 15 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN  
 AN 1981:4395 HCAPLUS  
 DN 94:4395  
 TI Manufacture of acrylonitrile  
 PA Asahi Chemical Industry Co., Ltd., Japan  
 SO Jpn. Kokai Tokkyo Koho, 4 pp.  
 CODEN: JKXXAF  
 DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 55104246	A2	19800809	JP 1979-11111	19790202
	JP 61044861	B4	19861004		
PRAI	JP 1979-11111	A	19790202		
AB	Acrylonitrile (I) [107-13-1]-containing gaseous product from ammoxidn. of propylene [115-07-1] was fed into bottom of a cooling tower divided into upper and lower sections into which cooling and stripping water was externally recycled sep. as countercurrents to the gas mixts. The cooling water in the lower section filled with Raschig rings was maintained at 75° so that it absorbed NH3 but not I. The initially cooled gas rose to the upper section of 5 trays. The I content in the cooling water reached a maximum of 4.5% at the 3rd tray. At this point, the condensate was removed from the tower and fed to extraction-distillation tower for further processing. This process provides a min. load on the extraction-distillation tower.				
IC	C07C121-32; C07C120-14				
CC	35-2 (Synthetic High Polymers)				
	Section cross-reference(s): 23				
ST	acrylonitrile recovery ammoxidn propylene				
IT	Ammoxidation (of propylene, to acrylonitrile, product recovery in)				
IT	115-07-1, reactions RL: RCT (Reactant); RACT (Reactant or reagent) (ammoxidn. of, to acrylonitrile, product recovery in)				
IT	107-13-1P, preparation RL: IMF (Industrial manufacture); PREP (Preparation) (manufacture of, by propylene ammoxidn., product recovery in)				
IT	107-13-1P, preparation RL: IMF (Industrial manufacture); PREP (Preparation) (manufacture of, by propylene ammoxidn., product recovery in)				
RN	107-13-1 HCAPLUS				
CN	2-Propenenitrile (9CI) (CA INDEX NAME)				



L36 ANSWER 16 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1981:3761 HCAPLUS

DN 94:3761

TI Separation of acetonitrile from crude olefinic unsaturated nitriles

IN Katsuta, Issei; Tanaka, Tetsuo

PA Asahi Chemical Industry Co., Ltd., Japan

SO Ger. Offen., 16 pp.

CODEN: GWXXBX

DT Patent

LA German

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 3003319	A1	19800807	DE 1980-3003319	19800130
	DE 3003319	C2	19850314		
	JP 55104244	A2	19800809	JP 1979-11109	19790202
	JP 61044860	B4	19861004		
	GB 2041931	A	19800917	GB 1980-2789	19800128

GB 2041931 B2 19830323  
US 4294665 A 19811013 US 1980-115865 19800128  
PRAI JP 1979-11109 A 19790202  
AB An apparatus was developed for separation of MeCN from the crude ammoxidn. products of propene or isobutene by passage through a quenching column, an absorption column (which operated with H<sub>2</sub>O), an extractive distillation column for separation of unsatd. nitrile, and a stripping column; the MeCN-containing vapor from the stripping column was condensed, regasified, and the MeCN recovered as a liquid via vapor-liquid separation  
IC C07C121-32; C07C121-18; C07C120-14  
CC 23-19 (Aliphatic Compounds)  
ST acetonitrile sepn olefinic nitrile  
IT 107-13-1P, preparation  
RL: PREP (Preparation)  
(separation of acetonitrile from crude product mixts. containing)  
IT 75-05-8P, preparation  
RL: PREP (Preparation)  
(separation of, from crude acrylonitrile product mixts.)  
IT 107-13-1P, preparation  
RL: PREP (Preparation)  
(separation of acetonitrile from crude product mixts. containing)  
RN 107-13-1 HCAPLUS  
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 17 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN  
AN 1980:472585 HCAPLUS  
DN 93:72585  
TI Acrylonitrile with low oxazole content  
IN Elischer, Stefan; Herberg, Gunther; Lienhard, Klaus; Wagner, Fritz  
PA SKW Trostberg A.-G., Fed. Rep. Ger.  
SO Ger. Offen., 10 pp.  
CODEN: GWXXBX  
DT Patent  
LA German  
FAN.CNT 1  
PATENT NO. KIND DATE APPLICATION NO. DATE  
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PI DE 2848512 A1 19800522 DE 1978-2848512 19781108  
DE 2848512 B2 19801127  
DE 2848512 C3 19811112  
PRAI DE 1978-2848512 A 19781108  
AB Oxazole (I) [288-42-6] content of acrylonitrile (II) [107-13-1] from olefin ammoxidn. is reduced to <5 ppm by washing the gaseous II product stream with water in an absorption column, removing II as overhead from the washed gas stream by distillation in a solvent extraction column, and removing a I-rich side stream from the lower part of the extraction column. The gaseous side stream is combined with the absorption water at the head of the absorption column, and the I is driven off by the residual gases at the top of the column and removed with them.  
IC C07C121-32; C07C120-14  
CC 35-2 (Synthetic High Polymers)  
Section cross-reference(s): 23  
ST oxazole removal acrylonitrile

IT 107-13-1P, preparation  
 RL: PUR (Purification or recovery); PREP (Preparation)  
 (purification of, oxazole removal in)

IT 288-42-6  
 RL: REM (Removal or disposal); PROC (Process)  
 (removal of, from acrylonitrile)

IT 107-13-1P, preparation  
 RL: PUR (Purification or recovery); PREP (Preparation)  
 (purification of, oxazole removal in)

RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 18 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1979:438893 HCAPLUS

DN 91:38893

TI Identification and determination of by-products of the acrylonitrile synthesis

AU Deutsch, K.; Schimke, D.; Neugebauer, B.; Bielicki, K. H.; Stoecker, J.

CS VEB Petrolchem. Komb. Schwedt, Schwedt, DDR-133, Ger. Dem. Rep.

SO Journal fuer Praktische Chemie (Leipzig) (1979), 321(1), 137-40  
 CODEN: JPCEAO; ISSN: 0021-8383

DT Journal

LA German

AB In the synthesis of  $\text{H}_2\text{C}:\text{CHCN}$  from  $\text{MeCH}:\text{CH}_2$ ,  $\text{NH}_3$ , and air in the gas phase, using an oxidation catalyst, numerous by-products were formed in addition to the desired products ( $\text{H}_2\text{C}:\text{CHCN}$ ,  $\text{MeCN}$ , and  $\text{HCN}$ ). These were extracted from the waste waters of the reactor gas quench column and the  $\text{MeCN}$  removal column, and fractions from distillation of the sump and identified by  $^1\text{H}$  NMR. Among the 44 such compds. identified (and in some cases quant. determined) were, besides the desired products, nicotinonitrile, pyrimidine derivs., fumaronitrile,  $\text{AcNH}_2$ , hydroquinone,  $\text{Me}_2\text{CO}$ ,  $\text{PrCN}$ ,  $\text{MeOH}$ , pyridine,  $\text{PhCN}$ , 2-furancarbonitrile,  $\text{AcOH}$ , and cyanohydrins of  $\text{Me}_2\text{CO}$ ,  $\text{HCHO}$ , and  $\text{MeCHO}$ .

CC 23-19 (Aliphatic Compounds)  
 Section cross-reference(s): 80

ST acrylonitrile synthesis byproduct; hydrogen cyanide synthesis byproduct; acetonitrile synthesis byproduct

IT 50-00-0P, preparation 60-35-5P, preparation 64-18-6P, preparation  
 64-19-7P, preparation 67-56-1P, preparation 67-64-1P, preparation  
 71-43-2P, preparation 75-07-0P, preparation 75-12-7P, preparation  
 75-86-5P 78-97-7P 79-06-1P, preparation 79-10-7P, preparation  
 100-47-0P, preparation 100-54-9P 107-02-8P, preparation 107-12-0P  
 107-16-4P 109-74-0P 109-75-1P 110-61-2P 110-67-8P 110-86-1P,  
 preparation 123-31-9P, preparation 126-98-7P 288-42-6P  
 592-51-8P 617-90-3P 764-42-1P 928-53-0P 1190-76-7P 2478-49-1P  
 4786-20-3P 5809-59-6P 70688-28-7P 70688-29-8P 70688-30-1P

RL: PREP (Preparation)  
 (by-product from synthesis of acrylonitrile, acetonitrile, and hydrocyanic acid)

IT 289-95-2DP, derivs.  
 RL: PREP (Preparation)  
 (by-products from synthesis of acrylonitrile, acetonitrile, and hydrocyanic acid)

IT 107-13-1P, preparation  
 RL: PREP (Preparation)

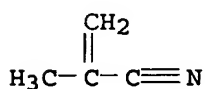
(identification and determination of by-products from synthesis of)

IT 70687-56-8P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of)

IT 74-90-8P, preparation 75-05-8P, preparation  
 RL: RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)  
 (synthesis of, by-products from)

IT 126-98-7P  
 RL: PREP (Preparation)  
 (by-product from synthesis of acrylonitrile, acetonitrile, and  
 hydrocyanic acid)

RN 126-98-7 HCAPLUS  
 CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



IT 107-13-1P, preparation  
 RL: PREP (Preparation)  
 (identification and determination of by-products from synthesis of)

RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 19 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN  
 AN 1974:52114 HCAPLUS  
 DN 80:52114  
 TI Waste treatment process based on the submerged combustion  
 technology  
 AU Tsuruta, Hidemasa  
 CS Nittetsu Chem. Eng. Ltd., Japan  
 SO Sekiyu Gakkaishi (1973), 16(8), 646-50  
 CODEN: SKGSAE; ISSN: 0582-4664  
 DT Journal  
 LA Japanese  
 AB A waste solution (chloride tar) formed during the production of vinyl chloride  
 monomers from C<sub>2</sub>H<sub>4</sub> is incinerated to recover HCl. The waste solution in  
 incinerated in a submerged combustion apparatus, and its waste heat is used to  
 concentrate a CaCl<sub>2</sub> solution to .apprx.60%. The resulting gas containing  
 .apprx.10% HCl is passed through an absorption column. A 15-18% HCl  
 recovered from the absorption column and the 60% CaCl<sub>2</sub> solution are supplied  
 to an extractive distillation column, from which a  
 gas containing .apprx.60-80% HCl is obtained. A portion of the  
 gas is recycled after condensation. The uncondensed HCl  
 gas is condensed at .apprx.0° and .apprx.2 kg/cm<sup>2</sup> to yield  
 a HCl gas containing <50 ppm H<sub>2</sub>O. The effluent  
 gas containing HCl 30-50 ppm and Cl<sub>2</sub> 10-20 ppm from the absorption  
 column is scrubbed with an alkali solution and discharged to the  
 atmospheric. The recovery of HCl is .apprx.97%. Processes for treating waste  
 solns. containing organic Na salts from caprolactam production and waste solution  
 containing  
 organic compds., cyanides, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> from acrylonitrile production are  
 described.

CC 60-2 (Sewage and Wastes)  
Section cross-reference(s): 35  
ST hydrogen chloride recovery waste; plastic recovery hydrogen chloride  
IT Wastes  
(from vinyl chloride manufacture, hydrogen chloride recovery from submerged  
combustion of)  
IT Waste gases  
(hydrochloride recovery from, from submerged combustion of vinyl  
chloride manufacture waste)  
IT Organic compounds, uses and miscellaneous  
RL: REM (Removal or disposal); PROC (Process)  
(removal of, from acrylonitrile and caprolactam manufacture effluents)  
IT Cyanides, uses and miscellaneous  
RL: REM (Removal or disposal); PROC (Process)  
(removal of, from acrylonitrile manufacture effluent)  
IT Combustion  
(submerged, of vinyl chloride manufacture waste, hydrogen chloride recovery  
from)  
IT 7783-20-2P, preparation  
RL: PREP (Preparation)  
(recovery of, from acrylonitrile manufacture effluent)  
IT 7647-01-0P, preparation  
RL: PREP (Preparation)  
(recovery of, of waste gas from submerged combustion of vinyl  
chloride manufacture waste)  
IT 75-01-4P, preparation  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(waste from manufacture of, hydrochloric acid recovery from submerged  
combustion of)  
IT 105-60-2P, preparation 107-13-1P, preparation  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(waste from manufacture of, treatment of)  
IT 107-13-1P, preparation  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(waste from manufacture of, treatment of)  
RN 107-13-1 HCAPLUS  
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 20 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN  
AN 1972:141524 HCAPLUS  
DN 76:141524  
TI Recovering acrylonitrile, hydrocyanic acid, and acetonitrile from  
aqueous solutions  
PA Standard Oil Co.  
SO Brit., 4 pp.  
CODEN: BRXXAA  
DT Patent  
LA English  
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	GB 1263213		19720209		
	US 3661723		19720000	US	
PRAI	JP 1969-40239		19690526		
AB	Acrylonitrile [107-13-1], hydrocyanic acid [74-90-8], and				

acetonitrile [75-05-8] are recovered from their aqueous solution (obtained by contacting the product mixture from a catalytic vapor phase reaction of propylene, NH<sub>3</sub>, and mol. O with an acidic solution to neutralize unreacted NH<sub>3</sub>) by adding CH<sub>3</sub>CN to bring the CH<sub>3</sub>CN concentration within the range 0.3-4 weight percent and subsequent distillation. Thus to an aqueous sulfuric acid extract containing CH<sub>2</sub>:CHCN 1.0, CH<sub>3</sub>CN 0.15, HCN 0.70, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 15 weight percent was added a 20% solution of CH<sub>3</sub>CN so that the mixture for dist. contained >0.5 weight percent but <10 weight percent CH<sub>3</sub>CN. A distillation column provided with 20 perforated trays gave an overhead composition CH<sub>2</sub>:CHCN 6, CH<sub>3</sub>CN 20, HCN 6, and water 68 weight percent; the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution removed at the bottom of the distillation column contained <10 ppm CH<sub>2</sub>:CHCN. Distns. without the addnl. CH<sub>3</sub>CN gave polymeric deposits at a fast rate, thus fouling the reboiler and the condenser of the distillation column.

IC C07C  
 CC 35 (Synthetic High Polymers)  
 ST acrylonitrile recovery; acetonitrile recovery; hydrogen cyanide recovery; hydrocyanic acid recovery; distn recovery acrylonitrile; manuf acrylonitrile  
 IT 74-90-8P 75-05-8P, preparation 107-13-1P, preparation  
 RL: PREP (Preparation)  
 (recovery of, from ammonia-propene reaction mixture)  
 IT 107-13-1P, preparation  
 RL: PREP (Preparation)  
 (recovery of, from ammonia-propene reaction mixture)  
 RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 21 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN  
 AN 1971:41950 HCAPLUS  
 DN 74:41950  
 TI Separating acrylonitrile from acetonitrile in gaseous mixtures resulting from the catalytic oxidation of propylene in the presence of ammonia  
 IN Bitners, Feliks; Brandt, Hans W.; Hausweiler, Arnold; Mayer, Adolf; Beilstein, Gunter M.  
 PA Erdoelchemie G.m.b.H.; Farbenfabriken Bayer A.-G.  
 SO Ger. Offen., 12 pp.  
 CODEN: GWXXBX  
 DT Patent  
 LA German  
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 1920761	A	19701112	DE 1969-1920761	19690424
	GB 1269195	A	19720406	GB 1970-1269195	19700413
	NL 7005762	A	19701027	NL 1970-5762	19700421
	BE 749500	A	19701026	BE 1970-749500	19700424
	FR 2046509	A5	19710305	FR 1970-15131	19700424
PRAI	DE 1969-1920761	A	19690424		

AB Acetonitrile was separated from an oxidation mixture of propylene with NH<sub>3</sub> by extractive distillation using a multitray column (95 trays). An aqueous washing containing MeCN, HCN, CH<sub>2</sub>:CHCN, EtCN and water was introduced to the 12-25 tray zone of the column which was continuously washed with warm countercurrent water to wash

down MeCN and to evaporate other gaseous components.

IC C07C

CC 23 (Aliphatic Compounds)

ST sepn acetonitrile; acetonitrile sepn; oxidn propylene; propylene oxidn; acrylonitrile sepn

IT 107-13-1P, preparation

RL: PREP (Preparation)

(from propene, purification in)

IT 75-05-8, uses and miscellaneous

RL: REM (Removal or disposal); PROC (Process)

(removal of, from acrylonitrile)

IT 107-13-1P, preparation

RL: PREP (Preparation)

(from propene, purification in)

RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 22 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1970:110841 HCAPLUS

DN 72:110841

TI Separation of acrylonitrile and acetonitrile

IN Ikeda, Yoneichi; Takeda, Tsukasa; Hattori, Michio; Kiyomiya, Yutaka

PA Nitto Chemical Industry Co., Ltd.

SO Ger. Offen., 44 pp.

CODEN: GWXXBX

DT Patent

LA German

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 1807654	B2	19740502	DE 1968-1807654	19681107
	DE 1807654	C3	19741219		
	GB 1239460	A	19710714	GB 1968-1239460	19681106
	US 3694322	A	19720926	US 1968-774133	19681107
PRAI	JP 1967-71839	A	19671108		
	JP 1968-28555	A	19680430		

AB An aqueous solution of acrylonitrile (I) and MeCN, obtained by known methods of preparing I, is extractively distilled with water to remove I as vapor; the aqueous MeCN from the base of the column is stream stripped to remove MeCN. The steam stripping is at 1.2-1.6 atmospheric instead of 1 atmospheric. Steam from the stripping column is condensed at  $\approx 100^\circ$ ; the pressure over the condensed liquid (water containing 20% MeCN) is reduced to give hot (e.g.,  $134^\circ$ ) vapor and liquid, which are recycled to the bottom and top, resp., of the extractive distillation column. Thus, I was separated from MeCN at 1.6 atm in the stripping column. Steam requirements in the extractive distillation and steam stripping columns were 95% and 63%, resp., of amts. required in sepn. in which the stripping column was operated at 1 atmospheric

IC C07C

CC 23 (Aliphatic Compounds)

ST sepn acrylonitrile acetonitrile; acetonitrile sepn acrylonitrile; acrylonitrile acetonitrile sepn

IT 107-13-1P, preparation

RL: PUR (Purification or recovery); PREP (Preparation)



(purification of, acetonitrile removal in)  
IT 75-05-8, uses and miscellaneous  
RL: REM (Removal or disposal); PROC (Process)  
(removal of, from acrylonitrile)  
IT 107-13-1P, preparation  
RL: PUR (Purification or recovery); PREP (Preparation)  
(purification of, acetonitrile removal in)  
RN 107-13-1 HCAPLUS  
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 23 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN  
AN 1970:89829 HCAPLUS  
DN 72:89829.  
TI Continuous separation of acrylonitrile and acetonitrile  
IN Schoenbeck, Rupert; Krzemicki, Kasimir  
PA Lentia G.m.b.H. Chem. und Pharm. Erzeugnisse-Industriebedarf  
SO Ger. Offen., 15 pp.  
CODEN: GWXXBX

DT Patent  
LA German

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 1920083	A	19700129	DE 1969-1920083	19690421
PRAI	DE 1969-1920083	A	19690421		

AB A process is described for continuous separation of MeCN from H<sub>2</sub>C:CHCN, obtained by reaction of propylene with NH<sub>3</sub> and O, by absorption of the H<sub>2</sub>O-soluble product in H<sub>2</sub>O, introduction of the solution into an extractive distillation system using H<sub>2</sub>O as the extracting agent, obtaining the I-free II at the head of the extraction distillation and the I azeotrope as a side stream, and separation of the I azeotrope from most of the H<sub>2</sub>O. The extractive distillation was conducted in a plate column and the I side stream was preferably removed above the 15th plate. Thus, a mixture of H<sub>2</sub>O 176, II 135, I 16, N 710, other gases 78, and other organic compds. (such as HCN and acrolein) 21 g was charged hourly to the absorption tower, washed with 6000 g water containing 5 g I and 17 g other organic compds., and 710 g N and 78 g other gases escaped at the top of the column/hr. The mixture at the bottom of the tower, containing II 135, I 21, H<sub>2</sub>O 6176, and other organic compds. 38 g, was heated to 88° and introduced into a 49-plate column 30 plates from the bottom. The column was loaded at the top with 3000 g water at 68°. A fraction containing H<sub>2</sub>O 5, II 133, and other organic compds. 15 g was separated/hr. A side stream was separated 20 plates from the bottom at 99° containing water 6671, II 2, I 21, and other organic compds. 23 g and conducted to a 30-plate column. At the top of the column at 72°, a mixture consisting of H<sub>2</sub>O 4, II2, I 16, and other organic compds. 1 g was separated/hr. At the base of the column, a mixture was separated containing H<sub>2</sub>O 6000 g, I5, and other organic compds. 17 g.

IC C07C

CC 23 (Aliphatic Compounds)

ST acrylonitrile acetonitrile sepn; acetonitrile acrylonitrile sepn

IT 107-13-1P, preparation

RL: PUR (Purification or recovery); PREP (Preparation)

(purification of, acetonitrile removal in)  
IT 75-05-8, uses and miscellaneous  
RL: REM (Removal or disposal); PROC (Process)  
(removal of, from acrylonitrile)  
IT 107-13-1P, preparation  
RL: PUR (Purification or recovery); PREP (Preparation)  
(purification of, acetonitrile removal in)  
RN 107-13-1 HCAPLUS  
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 24 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1970:78480 HCAPLUS

DN 72:78480

TI Separation of acrylonitrile and acetonitrile

PA Farbenfabriken Bayer A.-G.; Erdoelchemie G.m.b.H.

SO Fr., 7 pp.

CODEN: FRXXAK

DT Patent

LA French

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	FR 1571726		19690620	FR	
	DE 1618447			DE	
	GB 1218405			GB	

PRAI DE 19670624

AB A gaseous mixture of MeCN and CH<sub>2</sub>:CHCN (I) is washed with water and I is removed by extractive distillation while the MeCN is separated from the water by fractional distillation. The water containing any residual MeCN is recirculated to the washing stage. Thus, 54,800 normal l./hr of a gas (from the preparation of I by oxidation of propylene in the presence of NH<sub>3</sub>, containing I 3125, MeCN 320, and HCN 1415 kg) was pumped at 25° into a washing tower containing 45 separator plates. A solution (92,859 kg/hr) containing I 3100, MeCN 320, and HCN 1415 kg was withdrawn at the bottom of the tower, heated to 80°, and pumped into an extraction tower containing 72 plates. Water at 70° and 30,000 kg/hr was introduced at the head of the tower and steam at 12.7 tons/hr at the base. A gaseous mixture of I 3100, HCN 1390, H<sub>2</sub>O 2500, and MeCN 0.5kg/hr was withdrawn at the tower head and condensed and a solution of H<sub>2</sub>O 53,368, MeCN 309.5, and HCN 7 kg/hr was withdrawn at the bottom and passed into an extraction tower with 6.2 tons/hr steam. A mixture of MeCN 309.5, H<sub>2</sub>O 77.1, and HCN 7 kg/hr was obtained at the head of the extraction tower while water from the bottom was cooled to 70° and pumped to the top of the distillation column, and 70,000 kg/hr water containing 10 kg/hr MeCN at 70-100°, from the bottom of the distillation tower, was pumped to the washing tower.

IC C07C

CC 23 (Aliphatic Compounds)

ST acrylonitrile acetonitrile sepn; acetonitrile acrylonitrile sepn

IT 107-13-1P, preparation

RL: PREP (Preparation)

(recovery of, from mixts. with acetonitrile)

IT 75-05-8, uses and miscellaneous

RL: USES (Uses)  
 (separation of, from acrylonitrile)  
 IT 107-13-1P, preparation  
 RL: PREP (Preparation)  
 (recovery of, from mixts. with acetonitrile)  
 RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 25 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1970:54814 HCAPLUS

DN 72:54814

TI Separation of acrylonitrile from acetonitrile

PA Erdoelchemie G.m.b.H.; Farbenfabriken Bayer A.-G.

SO Fr., 6 pp.

CODEN: FRXXAK

DT Patent

LA French

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	FR 1569457		19690530	FR	
	DE 1618324			DE	
	GB 1239957			GB	
	US 3535849		19700000	US	
PRAI	DE		19670624		

AB Acrylonitrile (I) is separated from the gaseous mixture (containing HCN and MeCN as by-products) obtained in the reaction of propylene with NH<sub>3</sub>. The mixture is washed with hot water in a washing column, the aqueous solution of I MeCN, and HCN is withdrawn and subjected to extractive distillation, I and HCN are distilled and the hot aqueous MeCN solution residue is divided into 2 streams; the MeCN is recovered from 1 stream by steam stripping, and the other stream is recycled to the top of the washing column. The MeCN in this 2nd stream is entrained by the gases (propylene, propane, and carbon oxides) which escape during washing, and the gas stream is burned. Thus, a gas prepared by the known oxidation of propylene in the presence of N h<sub>3</sub> was passed (54,800 standard m<sup>3</sup>/hr) at 25° into a washing column. The gas contained I 3125, MeCN 320, and HCN 1415 kg. An aqueous solution (92,679 kg/hr) containing I 3100, MeCN 320, and HCN 1415 k g, taken from the base of the column, was heated to 80° and passed into the midpoint of a 65-plate extraction column, where it was contacted with 38 m<sup>3</sup>/hr hot water (obtained from the MeCN/hr was removed from the base and separated into 2 streams. One stream (70,000 kg water and 180 kg MeCN/hr) was cooled to 50-60° and recycled to the top of the washing column. The other stream (53,538 kg water/hr and 139.5 kg MeCN/hr) was passed into an extraction column. A mixture of 139.5 kg MeCN/hr and 34.9 kg water/hr was distilled off. The water (38 m<sup>3</sup>/hr) from the base of the column was cooled to 70° and recycled to the top of the column used for the extractive distillation of I.

IC C07C

CC 23 (Aliphatic Compounds)

ST acrytonitrile acetonitrile sepn; acetonitrile acrytonitrile sepn

IT 107-13-1P, preparation

RL: PREP (Preparation)  
(acetonitrile removal in)  
IT 75-05-8, uses and miscellaneous  
RL: REM (Removal or disposal); PROC (Process)  
(removal of, from acrylonitrile)  
IT 107-13-1P, preparation  
RL: PREP (Preparation)  
(acetonitrile removal in)  
RN 107-13-1 HCAPLUS  
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 26 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1969:430095 HCAPLUS

DN 71:30095

TI **Extractive distillation** for separating nitrites, peroxides, and their precursors from unsaturated nitriles saturated with water

IN Jordan, Jackie B.; White, Thomas R.

PA Standard Oil Co.

SO U.S., 4 pp.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 3442771	A	19690506	US 1967-661087	19670816
PRAI	US 1967-661087	A	19670816		

AB The purpose of this invention is to remove trace nitrite impurities and their precursors from the crude acrylonitrile product obtained from an **extraction distillation** column. The crude nitriles are **distilled** as an azeotropic mixture of the nitrile and H<sub>2</sub>O, both phases of which contain the unwanted impurities. As the **distillate** is partially condensed, an **alkaline alkali** metal salt solution, preferably an alkali metal salt of H<sub>2</sub>CO<sub>3</sub>, such as a 1-5% solution by weight of Na<sub>2</sub>CO<sub>3</sub>, is injected into the **distillate**. This contacts both the organic and **aqueous** phases and exts. the impurities from the organic phase to the **aqueous** phase and there reacts with the impurities. The organic phase, containing the desired nitriles, is drawn off for purification. The trace impurities must be removed from the acrylonitrile solution since these impurities jeopardize many of the polymerization reactions in which the acrylonitrile is used as a monomer.

IC B01D

INCL 203033000

CC 23 (Aliphatic Compounds)

ST acrylonitrile purifn

IT 14797-65-0 14915-07-2, uses and miscellaneous

RL: REM (Removal or disposal); PROC (Process)

(removal of, from acrylonitrile)

IT 107-13-1P, preparation

RL: PREP (Preparation)

(separation of, from nitrite impurities)

IT 107-13-1P, preparation

RL: PREP (Preparation)

(separation of, from nitrite impurities)

RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 27 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1969:57186 HCAPLUS

DN 70:57186

TI Recovery and purification of acrylate and methacrylate esters by  
**extractive distillation with water**

IN Hougland, John W.; Wisniewski, John C.

PA Standard Oil Co.

SO U.S., 4 pp.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 3420751	A	19690107	US 1967-624308	19670320
	GB 1222993	A	19710217	GB 1968-1222993	19680220
	FR 1571398	A	19690620	FR 1968-1571398	19680319
PRAI	US 1967-624308	A	19670320		

AB Mixts. containing alcs., unsatd. nitriles, unsatd. acids, **water**, and esters of unsatd. carboxylic acids are separated by **extractive distillation with water**. Preferably, the mixture is passed through an ether column, where the desired ester is removed with the side draw, and then through an **extractive distillation** column, from which the ester is removed as overhead in its **water** azeotrope. The overhead from the ether column and the bottoms from the **extractive distillation** column are passed through an alc. column, from which the reflux is partially returned to an esterification reactor and the bottoms, consisting mainly of **water**, is used in the **extractive distillation**. The wet ester from the **extractive distillation** is separated in a **decanter** and added at about the middle of a drying column, from which ethers and unsatd. nitriles are withdrawn as overhead and the desired ester, as bottoms containing only a small amount of **water**. **Water** from the **decanter** is refluxed to the top of the **extractive distillation** column. An example in which Et acrylate was separated from a mixture also containing Et<sub>2</sub>O, EtOH, acrylonitrile, **water**, acrylic acid, and β-ethoxyethyl propionate was given. This process gives good recovery, and the apparatus requires a min. number of columns and can be used for various mixts.

INCL 203082000

CC 23 (Aliphatic Compounds)

ST ethyl acrylate recovery purifn; acrylate ethyl recovery purifn; recovery purifn ethyl acrylate; purifn recovery ethyl acrylate; **extractive distn acrylates water; distn extractive acrylates water**

IT 64-17-5P, preparation 79-10-7P, preparation 107-13-1P,  
preparation 140-88-5P, preparation

RL: PREP (Preparation)

(separation of, from acrylic acid derivs.)

IT 14272-48-1

RL: PROC (Process)

(separation of, from mixts.)  
 IT 107-13-1P, preparation  
 RL: PREP (Preparation)  
 (separation of, from acrylic acid derivs.)  
 RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 28 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1968:507345 HCAPLUS

DN 69:107345

TI Cellulose copolymers

IN Pesek, Miroslav; Jarkovsky, Jaroslav

SO Czech., 6 pp.

CODEN: CZXXA9

DT Patent

LA Czech

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CS 125269		19671215	CS	19660418

AB Polymerization was carried out by irradiation (0.001-20.0 Mev., intensity of irradiation

0.1 r./sec.-500 Mr./sec. and dosing 100 rads-10 megarads) in H<sub>2</sub>O or dilute H<sub>2</sub>O<sub>2</sub>. When excess H<sub>2</sub>O<sub>2</sub> was removed the material was treated with vapors of vinyl monomer at temps. >40°. Thus, 0.2 g. 1.4-denier viscose staple was treated with 10 cc. 1% H<sub>2</sub>O<sub>2</sub> and after 0.5 hr. the product was irradiated with γ 60Co at 0.362 Mr./hr. to obtain 0.854 megarad. Then excess H<sub>2</sub>O<sub>2</sub> was removed in vacuo, the staple was washed with distilled H<sub>2</sub>O, H<sub>2</sub>O was removed and irradiated staple was introduced into vapors on a boiling mixture 1:1 styrene-H<sub>2</sub>O with 0.05% methylene blue for 2 hrs. at 99°. Then the staple was extracted with C<sub>6</sub>H<sub>6</sub> for 24 hrs. About 63% of styrene was bound with the activity 98%.

IC C08F

CC 36 (Plastics Manufacture and Processing)

ST cellulose copolymers; styrene cellulose copolymers; vinyl cellulose copolymers

IT Polymerization

(graft, by gamma irradiation, of vinyl compds. on cellulose and rayon)

IT Vinyl compounds, preparation

RL: PREP (Preparation)

(polymers with cellulose and rayon, by gamma irradiation)

IT Gamma rays, chemical and physical effects

(polymerization (graft) by, of vinyl compds. on cellulose and rayon)

IT Rayon, preparation

RL: PREP (Preparation)

(vinyl compound-grafted, by gamma irradiation)

IT 80-62-6P, Methacrylic acid methyl ester, preparation

RL: PREP (Preparation)

(polymers with cellulose and rayon, by gamma irradiation)

IT 79-41-4P, Methacrylic acid, preparation 100-42-5P, Styrene, preparation

107-13-1P, Acrylonitrile, preparation

RL: PREP (Preparation)

(polymers with rayon, graft, by gamma irradiation)

IT 9004-34-6P, preparation

RL: PREP (Preparation)  
 (vinyl compound-grafted, by gamma irradiation)  
 IT 107-13-1P, Acrylonitrile, preparation  
 RL: PREP (Preparation)  
 (polymers with rayon, graft, by gamma irradiation)  
 RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 29 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1968:505946 HCAPLUS

DN 69:105946

TI Extractive distillation of unsaturated nitriles

IN Lovett, Gordon H.

PA Monsanto Co.

SO U.S., 8 pp.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 3399120	A	19680827	US 1965-512651	19651209
	IL 27008	A1	19700521	IL 1966-27008	19661204
	BE 690877	A	19670608	BE 1966-690877	19661208
	NL 6617310	A	19670612	NL 1966-17310	19661209
	ES 334328	A1	19680201	ES 1966-334328	19661209
PRAI	US 1965-512651	A	19651209		

AB An extractive distillation process for the recovery of olefinically unsatd. nitriles, especially acrylonitrile (I), from crude nitrile mixts. is described which requires .apprx.33% less steam than a conventional extractive distillation process. As in the conventional process, the crude nitrile mixture is fed to a 60-100 tray column. H<sub>2</sub>O is added at the top of the column, causing the H<sub>2</sub>O-miscible impurities to be carried down the column and H<sub>2</sub>O-I to pass overhead. The H<sub>2</sub>O-rich bottoms from the column are passed to a 40-60-tray stripping column where the impurities are taken overhead and condensed, and the H<sub>2</sub>O layer is returned to the column. The column bottoms, mainly H<sub>2</sub>O, are returned to the top of the first column. In the conventional process, both columns are heated with open steam. In the process of this invention, steam is fed only to the bottom of the stripping column in an amount about 10% greater than in the prior art. A portion of the vapors from just above the feed point in the stripping column is drawn off and fed to the bottom of the first column. E.g., a stream containing 7.5% I, 1.3% MeCN, 1.3% HCN, and 89.9% H<sub>2</sub>O was fed to the 40th tray of the first column at .apprx.180°F. A mixture of H<sub>2</sub>O and I of the same composition as in the conventional process was taken overhead. Bottoms were fed to the 60th tray of the stripping column. and vapors were taken from above the 60th tray and fed below the first tray of the first column. Steam was fed to the bottom of the stripping column at a rate of 6500 lb./hr. compared to 5700 lb./hr. plus 4030 lb./hr., for the first column, in the conventional process.

INCL 203084000

CC 23 (Aliphatic Compounds)

ST ext distn acrylonitrile; acrylonitrile ext

**distn; distn acrylonitrile ext; unsatd**  
**nitriles ext distn; nitriles ext**  
**distn unsatd; purifn acrylonitrile**  
IT 107-13-1P, preparation  
RL: PUR (Purification or recovery); PREP (Preparation)  
(purification of, apparatus for)  
IT 107-13-1P, preparation  
RL: PUR (Purification or recovery); PREP (Preparation)  
(purification of, apparatus for)  
RN 107-13-1 HCAPLUS  
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 30 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN  
AN 1968:12444 HCAPLUS  
DN 68:12444  
TI Production of acrylonitrile from propylene  
AU Lichtenberger, R.  
CS Centre Rech. Lyon, Lyon, Fr.  
SO Revue de l'Association Francaise des Techniciens du Petrole (1967), No.  
183, 29-35  
CODEN: RAFTAX; ISSN: 0004-5470  
DT Journal  
LA French  
AB The Uguine-Distillers process is described and compared with  
other processes for manufacturing CH<sub>2</sub>:CHCN (I). A mixture of 5-8% by volume C<sub>3</sub>H<sub>6</sub>,  
5-10% NH<sub>3</sub>, 10-30% H<sub>2</sub>O, and air is fed over an unspecified  
catalyst at 400-80°, with a contact time of a few sec. Under  
optimum conditions the NH<sub>3</sub>/C<sub>3</sub>H<sub>6</sub> ratio is 1.0-1.2, and 50-60% C<sub>3</sub>H<sub>6</sub> is  
converted to I, 1-2% to MeCN, 5-7% to HCN, 1-7% to CH<sub>2</sub>:CHCHO (II), and  
16-20% to CO and CO<sub>2</sub>. The gaseous product is washed with H<sub>2</sub>SO<sub>4</sub>  
to remove NH<sub>3</sub>, and then with H<sub>2</sub>O to remove organic compds. The  
cyanohydrin of II and HCN are separated by fractional distillation, and  
MeCN by extractive distillation with H<sub>2</sub>O. A  
flowsheet of the plant is given.  
CC 23 (Aliphatic Compounds)  
ST ACRYLONITRILE MANUF; PROPYLENE TO ACRYLONITRILE  
IT 115-07-1, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(ammoxidn. of)  
IT 107-13-1P, preparation  
RL: PREP (Preparation)  
(manufacture of, from propene)  
IT 7664-41-7, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(oxidative, with propene)  
IT 107-13-1P, preparation  
RL: PREP (Preparation)  
(manufacture of, from propene)  
RN 107-13-1 HCAPLUS  
CN 2-Propenenitrile (9CI) (CA INDEX NAME)





L36 ANSWER 31 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1967:499637 HCAPLUS

DN 67:99637

TI Reclamation of ethylene glycol used in the purification of acrylonitrile

IN Wirtz, Peter; Sennewald, Kurt

PA Knapsack A.-G.

SO Ger., 4 pp. Addn. to Ger. 1189071

CODEN: GWXXAW

DT Patent

LA German

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 1250427		19670921	DE	19641204
AB	Addition to Ger. 1,189,071 (CA 62: 16055h). The reclamation of ethylene glycol (I), used in the purification of crude acrylonitrile (II), is carried out according to a previous patent (loc. cit.) with the modification that p-toluenesulfonic acid (III) catalyst is converted with water-free NH <sub>3</sub> , amine, or alkali or alkaline earth hydroxide to the corresponding salt before using it in the decomposition of the addition products of I and Me vinyl ketone (IV) found in the still residue. Thus, to neutralize III present in the distilled residue, NH <sub>3</sub> was introduced into the neutralization vessel. A sample of the treated residue treated with water had a pH of 7.5. The mixture contained the addition product of I and IV, and NH <sub>3</sub> was passed through a preheating arrangement into a distillation column and heated to 140°. Within 0.5 min. at 140°/200 mm. the still residue was completely free from IV and any remaining II.				
IC	C07C				
CC	23 (Aliphatic Compounds)				
ST	ACRYLONITRILE PURIFN; ETHYLENE GLYCOL RECOVERY				
IT	18360-27-5P, 2-Propanol, 1,1'-[[2-(2-hydroxyethoxy)ethyl]imino]di- RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of)				
IT	107-13-1P, preparation RL: PUR (Purification or recovery); PREP (Preparation) (purification of, ethylene glycol recovery from)				
IT	107-21-1P, preparation RL: PREP (Preparation) (recovery of, during acrylonitrile purification)				
IT	107-13-1P, preparation RL: PUR (Purification or recovery); PREP (Preparation) (purification of, ethylene glycol recovery from)				
RN	107-13-1 HCAPLUS				
CN	2-Propenenitrile (9CI) (CA INDEX NAME)				



L36 ANSWER 32 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1961:7793 HCAPLUS

DN 55:7793

OREF 55:1473d-i,1474a-i,1475a-b

TI The mechanism of organomercurial oxidation by mercuric salts

AU Robson, J. H.; Wright, George F.

CS Univ. Toronto

SO Canadian Journal of Chemistry (1960), 38, 1-20

CODEN: CJCHAG; ISSN: 0008-4042

DT Journal

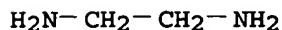
LA Unavailable

AB cf. CA 50, 10015h. The oxidation of certain organomercuric nitrates or acetates by inorg. mercuric salts led to ether, alc., aldehyde, acid, and ester derivs. of the organic compound. The observations that the oxidation was inhibited by O, accelerated by acids, yielded esters even in the presence of much H<sub>2</sub>O, that the system polymerized acrylonitrile, and that the same products were formed when pernitrous acid replaced the inorg. salt were evidences of a free radical reaction. Kinetic studies showed that radicals were involved in a self-regenerating chain in which the active monomeric mercurous salt was thought to be the carrier. Oxidation of cyclohexylmercuric nitrate (I) (cyclohexyl = C<sub>6</sub>H<sub>11</sub>) by Hg(NO<sub>3</sub>)<sub>2</sub> in MeOH gave 31% C<sub>6</sub>H<sub>11</sub>ONO<sub>2</sub> (II) and 8% C<sub>6</sub>H<sub>11</sub>OMe. I (0.0313 mole) (freshly prepared from the chloromercurial and AgNO<sub>3</sub>) in 450 ml. dry MeOH was treated with 0.0313 mole of both Hg(NO<sub>3</sub>)<sub>2</sub> and absolute HNO<sub>3</sub> 38 hrs., cooled to 0°, diluted with 400 ml. H<sub>2</sub>O, 15 ml. 5M NaCl added and the whole filtered to give 12.79 g. CHCl<sub>3</sub>-insol. HgCl. The filtrate extracted with Et<sub>2</sub>O and the extract washed with dilute base and H<sub>2</sub>O, dried, and distilled gave a fraction (1.06 g.), b<sub>2-3</sub> 24-41°, which was chromatographed on silicic acid, eluted with hexane, and analyzed by infrared spectrum. Oxidation of I in H<sub>2</sub>O gave 21% II, 40% C<sub>6</sub>H<sub>11</sub>OH (III), and a trace of formylcyclopentane (IV). I (20.00 g.) in 140 ml. H<sub>2</sub>O, stirred 16 hrs. with 18.82 g. Hg(NO<sub>3</sub>)<sub>2</sub> and 7.5 ml. 8M HNO<sub>3</sub>, was extracted with Et<sub>2</sub>O and 2.51 g. metallic Hg separated from the aqueous phase and, by addition of excess NaCl, 24.5 g. HgCl. Et<sub>2</sub>O exts. washed with dilute base, H<sub>2</sub>O, dried, and distd. gave 2 fractions (1) (0.38 g.), b<sub>37</sub> 15-40°, and (2) (4.14 g.), b<sub>42-3</sub> 65-84°. Infrared spectra showed the fractions to be nearly identical mixts. of II and III (the OH band at 3450 cm.<sup>-1</sup> was used and the covalent nitrate band at 1650 cm.<sup>-1</sup>). The 2,4-dinitrophenylhydrazine derivative (V) (12 mg.) of IV, m. 149-152°, resulted from treatment of 0.10 g. fraction 2 with dinitrophenylhydrazine (DNPH). Substitution of I by III gave no II under comparable conditions. A similar 10-hr. aqueous oxidation of benzylmercuric nitrate (0.0306 mole) gave 2.46 g. yellow oil on concentration of the Et<sub>2</sub>O exts. A portion (1.000 g.) chromatographed on 2:1 silicic acid-Celite (activated at 150°) gave 2 fractions, (1) (0.360 g.), pos. test for carbonyl and nitrate ester and (2), neg. test for ester. Fraction 1, in 15 ml. dry EtOH, treated 15 hrs. with 1.43 ml. glacial HOAc and 0.59 g. Girard P reagent, poured into 50 ml. cold H<sub>2</sub>O containing 1.19 g. Na<sub>2</sub>CO<sub>3</sub>, extracted cold with CHCl<sub>3</sub>, the exts. washed with H<sub>2</sub>O, dried over MgSO<sub>4</sub>, and concentrated gave 0.288 g. PhCH<sub>2</sub>ONO<sub>2</sub>, m. -23 to -17.5°. In an identical oxidation, the oil obtained after Et<sub>2</sub>O extraction was distilled; a 2.36 g. fraction, b<sub>30</sub> 65-100°, showed a trace amount of PhCHO (DNPH), deposited about 20 mg. PhCO<sub>2</sub>H, and a 0.47 g. sample gave 0.39 g. phenylurethan of PhCH<sub>2</sub>OH. A suspension, prepared at 0°, of 300 ml. MeOH, 300 ml. H<sub>2</sub>O, 0.06 mole I, 0.009 mole 8M HNO<sub>3</sub>, and 0.09 mole 90% H<sub>2</sub>O<sub>2</sub> was warmed to and maintained at 25° while 0.066 mole NaNO<sub>2</sub> in 60 ml. H<sub>2</sub>O was slowly added in 20 min. The serial addition of like amts. of HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and NaNO<sub>2</sub> was repeated thrice. The mixture was extracted with Et<sub>2</sub>O, the exts. dried, and distilled to give 5.51 g. oil, which gave the V of cyclohexanone (VI), m. 150-3°, and (by infrared spectra) yields of 30% and 25%, resp., III and II. Hg(NO<sub>3</sub>)<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> (0.01 mole each) in 40 ml. dry MeOH gave a neg. Hg<sup>+</sup> test after 4 hrs. An exothermic reaction occurred on addition of 3-4 mg. FeSO<sub>4</sub>·7H<sub>2</sub>O; after 20 hrs. stirring and addition of 7 ml. 8M HNO<sub>3</sub>, HgCl and HgO were recovered, with NaCl and NaOH, resp., in 60 and 40% yield. The same procedure in H<sub>2</sub>O produced no Hg<sup>+</sup> salt after 10 hrs. Hg(NO<sub>3</sub>)<sub>2</sub> (0.82 millimole) in 5.0 ml. dry MeOH stirred 12 hrs. with 5.0 ml.

0.17M solution of isobutyryl peroxide in MeOH gave a neg. test for peroxide, 0.12 g. HgCl<sub>2</sub>, but no HgO. A series of 10 organomercuric nitrates bleached a MeOH solution of diphenylpicrylhydrazyl (VII), indicating radical formation arising in the organomercurial. Bleaching rates were studied, e.g., 0.005 mole I in 40 ml. MeOH was added to 16.0 mg. VII in 400 ml. MeOH, made up to 500 ml., and % transmittance at 510 mμ measured with time. With mercurial in large excess, 1st-order rates were observed. A rough correlation of relative rates was found between the above 1st-order bleaching rates and the 2nd-order rates of oxidation of the same mercurials with Hg(NO<sub>3</sub>)<sub>2</sub> as in the example. I (0.00313 mole) in 2.5 ml. dry MeOH was added to 0.00313 mole Hg(NO<sub>3</sub>)<sub>2</sub> in 10 ml. MeOH, 0.00626 mole absolute HNO<sub>3</sub> added and immediately diluted to 50.00 ml. with MeOH. Aliquots (5.0 ml.) were transferred to tared centrifuge tubes, stoppered, thermostated at 25°, and analyzed by adding 4 ml. 2M HCl, centrifuging after 10 min., washing the precipitate with 5 ml. portions H<sub>2</sub>O, MeOH, and CHCl<sub>3</sub>, drying the solids at 110° and finally at 56° at 1 mm., and weighing as HgCl<sub>2</sub>. Cyclohexene (VIII) (0.00625 mole) was added to 0.0125 mole HgO and 0.050 mole HNO<sub>3</sub> in 23 ml. H<sub>2</sub>O, shaken 5 min., and 0.0125 mole freshly distilled acrylonitrile added. Turbidity developed in 40 min. and 0.026 g. polyacrylonitrile (IX) (4% of monomer) was recovered in 3 hrs. The same procedure gave 7% IX in 3 hrs. when the system was deaerated. The same procedure plus 0.65 millimole methylenediacrylamide gave 0.176 g. IX in 3 hrs. These polymers were equivalent to IX from a mixture of 0.01 mole acrylonitrile, 20 ml. H<sub>2</sub>O, 0.10 ml. 90% H<sub>2</sub>O<sub>2</sub>, 1-2 mg. FeSO<sub>4</sub>·7H<sub>2</sub>O (no visible change in the system in 1 hr.), and 2 ml. 8M HNO<sub>3</sub>; 0.28 g. IX was obtained in 12 hrs. Treatment of VIII (0.00625 mole) with an equimolar amount of Hg(NO<sub>3</sub>)<sub>2</sub> (from HgO and 1.57 ml. concentrated HNO<sub>3</sub>) in 23 ml. H<sub>2</sub>O gave a neg. test for Hg<sup>++</sup> in 30 min.; addition of 0.0125 mole acrylonitrile gave no measurable amount of IX in 1 day. Reactions of organomercuric acetates with Hg(OAc)<sub>2</sub> were much slower than the nitrates but the same type of product was obtained. Peracetic acid (0.05 mole) in CHCl<sub>3</sub> added to 0.01 mole cyclohexylmercuric acetate in 20 ml. dry MeOH and refluxed 7 hrs. gave a neg. peroxide test. The amount of HgOAc filtered off and converted to calomel (KCl) was 0.20 g.; the filtrate was diluted to 80 ml. and extracted with CHCl<sub>3</sub>. The aqueous phase gave 1.58 g. HgO (NaOH); the CHCl<sub>3</sub> phase (distilled) gave 0.74 g. VI. Also, α-2-hydroxycyclohexylmercuric acetate oxidized with Fenton's reagent gave 23% IV and 23% 2-chloromercuricyclohexanone (X) (x-ray pattern given). Thus, a system of 0.10 mole VIII, 0.10 mole Hg(OAc)<sub>2</sub>, and 200 ml. H<sub>2</sub>O gave a neg. test for Hg<sup>++</sup> salt after stirring 2 hrs. Over a 2-hr. period, 10 ml. H<sub>2</sub>O containing 0.10 mole H<sub>2</sub>O<sub>2</sub> and 0.10 mole FeSO<sub>4</sub>·7H<sub>2</sub>O were added simultaneously and equivalently, the suspension was stirred 68 hrs., extracted with Et<sub>2</sub>O, and the dried exts. distilled to give 1.19 g. IV, b. 130-8° (via V, m. 153-5°). The aqueous phase was treated with 0.10 mole 5M NaCl, and the precipitate, after drying, extracted with 150 ml. CHCl<sub>3</sub> to give 7.07 g. CHCl<sub>3</sub>-soluble solid, m. 138-40° (decomposition). The compound was assumed to be X. Hg(OAc)<sub>2</sub> and Hg(NO<sub>3</sub>)<sub>2</sub> in MeOH were reduced to Hg<sup>+</sup> (14 and 36%, resp.) in 80-90 hrs. at 50°. Acids, especially BF<sub>3</sub>·Et<sub>2</sub>O, catalyzed the reaction. Reduction rates in the system Hg(OAc)<sub>2</sub> (0.10M) in MeOH were  $K = 2.08 \times 10^{-4}$  and  $3.30 \times 10^{-4}$  min.<sup>-1</sup> with BF<sub>3</sub>·Et<sub>2</sub>O concns. at 0.02M and 0.04M, resp. Higher acid concns. did not increase the rate. Disappearance of Hg(OAc)<sub>2</sub> was determined by volumetric analysis for Hg<sup>++</sup> salt with KI and Hg(NO<sub>3</sub>)<sub>2</sub> (the acid interfered with analysis by thiocyanate). The Hg(OAc)<sub>2</sub> reduction rate ( $2.08 \times 10^{-4}$  with 20 mole-% BF<sub>3</sub>·Et<sub>2</sub>O) was not altered in the presence of the methoxymercurials of trans-stilbene (several concns.) and of β,β-dimethylstyrene. Thus, the rate-determining step in the acid-catalyzed oxidation was the oxidation-reduction of the inorg. salt in MeOH. An induction period indicated

radical participation. The influence of O was shown. The system  $\text{Hg}(\text{OAc})_2$  (0.005 mole) and 0.126 ml.  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  in 100 ml. dry MeOH, stirred and maintained at  $26-7^\circ$ , was studied under 17-19 lb. absolute O pressure (rate negligible), under air ( $K = 1.97 + 10^{-4} \text{ min.}^{-1}$ ), and after 4 deaerations ( $K = 9.28 + 10^{-4} \text{ min.}^{-1}$ ). Changes in ultraviolet absorption spectra with time of  $\text{Hg}(\text{NO}_3)_2$  and  $\text{Hg}(\text{OAc})_2$  in MeOH were given both with and without  $\text{HNO}_3$ . 27 references.

- CC 10D (Organic Chemistry: Alicyclic Compounds)  
 IT Alcohols  
 Aldehydes  
 Esters  
 Ethers  
 (from organomercury compound oxidation)  
 IT Polymerization  
 (of acrylonitrile)  
 IT Oxidation  
 (of mercury organic compds. by mercuric salts)  
 IT Reaction kinetics and(or) velocity  
 (of oxidation, of organomercury compds.)  
 IT Mercury, 2-methoxycyclohexyl-, nitrate  
 Mercury, butyl-, nitrate  
 (kinetics of reactions of)  
 IT Mercury, benzyl-, nitrate  
 Mercury, isopropyl-, nitrate  
 Mercury, propyl-, nitrate  
 (reaction kinetics of)  
 IT Mercury, cyclohexyl-  
 (salts, oxidation of, mechanism of)  
 IT Mercury, (2-methoxy-1,2-diphenylethyl)-  
 Mercury, [ $\alpha$ -(1-methoxy-1-methylethyl)benzyl]-  
 (salts, reaction kinetics of)  
 IT 7439-97-6, Mercury  
 (compds., oxidation by  $\text{Hg}(\text{II})$  salts, mechanism of)  
 IT 100-52-7, Benzaldehyde  
 (formation of, from benzylmercury nitrate oxidation)  
 IT 108-94-1, Cyclohexanone 2108-66-9, Cyclohexyl nitrate  
 (formation of, from cyclohexylmercury nitrate)  
 IT 15285-42-4, Benzyl nitrate  
 (from benzylmercury nitrate oxidation)  
 IT 872-53-7, Cyclopentanecarboxaldehyde 931-56-6, Ether, cyclohexyl methyl  
 (from cyclohexylmercury nitrate oxidation)  
 IT 62-53-3, Aniline 100-46-9, Benzylamine 107-15-3,  
 Ethylenediamine 124-09-4, 1,6-Hexanediamine 7664-41-7, Ammonia  
 90952-94-6, Cyclohexanol, 2-(acetoxymethyl)-  
 (oxidation of)  
 IT 107-13-1, Acrylonitrile  
 (polymerization of)  
 IT 14839-64-6, Mercury, 2-oxocyclohexyl-, chloride 14839-64-6,  
 Cyclohexanone, 2-(chloromethyl)-  
 (preparation of)  
 IT 7439-97-6, Mercury  
 (salts, organomercury compound oxidation by)  
 IT 107-15-3, Ethylenediamine  
 (oxidation of)  
 RN 107-15-3 HCAPLUS  
 CN 1,2-Ethanediamine (9CI) (CA INDEX NAME)



IT 107-13-1, Acrylonitrile  
(polymerization of)  
RN 107-13-1 HCAPLUS  
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 33 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1960:7169 HCAPLUS

DN 54:7169

OREF 54:1489b-i,1490a-i,1491a-f

TI The addition of acrylonitrile to pyrroles

AU Fischer, Hans; Loewe, Heinz

CS Tech. Hochschule, Munich, Germany

SO Ann. (1958), 615, 124-36

DT Journal

LA Unavailable

AB This is a study of the addition of acrylonitrile to pyrrole derivs. in order to make various pyrrolepropionic acids, with Na alcoholates as catalyst. Acrylonitrile was added to 2,4-dimethyl-5-carbethoxypyrrole to form 2,4-dimethyl-5-carbethoxy-1-pyrrolepropionitrile; nucleus substitution of this was investigated. Certain condensation reactions and the saponification of the nitrile group were investigated. The behavior of the new pyrrole derivs. which were obtained from 2,4-dimethyl-5-carbethoxypyrrole was given. The following 1-pyrrolepropionitriles were obtained by addition of acrylonitrile: 2,4-dimethyl-5-carbethoxy- (I), 2,4-dimethyl-3-formyl-5-carbethoxy- (II), 2,4-dimethyl-3,5-dicarbethoxy- (III), 2,4-dimethyl-3-acetyl-5-carbethoxy- (IV), 2,3-dimethyl-5-formyl-4-carbethoxy- (V), 2,3-dimethyl-5-carbethoxy- (VI), 2-methyl-5-carbethoxy- (VII), 2-methyl-3-carbethoxy- (VIII), 2,4-dimethyl-3-ethyl- (IX), 2,4-dimethyl- (X), 2,4-dimethyl-5-carbethoxy-3-{ $\beta$ -[carbethoxy(2-cyanoethyl)amino]ethyl}- (XI). Acrylonitrile could not be added to 2,4-dimethyl-5-carbethoxy-3-pyrrolepropionic acid and to 2,4-dimethyl-5-carbethoxy-3-nitrovinylpyrrole. Rearrangement of the propionitrile residue from N to C did not take place. Under the action of sodium alcoholate at 150° the propionitrile residue was again split out. II showed the normal reaction of pyrrole aldehyde unsubstituted on the N. It gave an oxime, a semicarbazone, a phenylhydrazone, and an azlactone, condensed with malonic acid to 2,4-dimethyl-5-carbethoxy-1-( $\beta$ -cyanoethyl)-3-pyrroleacrylic acid (XII), reduced to the propionic acid analog (XIII) and condensed with nitro-methane to 2,4-dimethyl-5-carbethoxy-3-(2-nitrovinyl)-1-pyrrolepropionitrile (XIV), which was converted into XIV 3-( $\beta$ -hydroxyiminoethyl) analog (XV) and then with Ac<sub>2</sub>O into XIV 3-cyanomethyl analog (XVI). II aldoxime gave with Ac<sub>2</sub>O the acetylated oxime, while the corresponding material with the unsubstituted N was converted smoothly into the nitrile. The 1-(p-tolyl) analog of these aldoximes was only converted into the ecetyl compound 2,4-Dimethyl-5-carbethoxypyrrole (7.5 g.) is dissolved in 10 cc. freshly distilled acrylonitrile and colled to give a stiff pate. Into the colled mass was added dropwise 10 cc. 5% NaOEt in absolute alc., with shaking until small bubbles appeared. The mixture was colled, after 1 hr. triturated with 50 cc. Et<sub>2</sub>O, the solid filtered off and exhaustively extracted with Et<sub>2</sub>O, dried, evaporated, and the residue fractionated to give  $\beta$ -ethoxypropionitrile, b<sub>10</sub> 61-3°, 2,4-dimethyl-5-carbethoxypyrrole, b<sub>10</sub> 130-50°, and I, b<sub>10</sub> 175-85°. I, obtained in 50-80% yield, m. 84.5° (MeOH). I (0.8 g.) heated 10

hrs. in a pressure tube at 150° with 4 cc. 7.5% NaOMe in absolute alc. gave 2,4-dimethyl-5-carbethoxypyrrole, m. 123° (alc.). The same results were obtained with 1-propionamide analog. I (1.5 g.) in 5 cc. glacial AcOH treated with 0.3 cc. Br in 2 cc. glacial AcOH yielded 1.5 g. 3-bromo-2,4-dimethyl-5-carbethoxy-1-pyrrolepropionitrile m. 85-8° (EtOH). I (18 g.) was suspended in 75 cc. absolute Et2O and 25 cc. CHCl3; for removal of alc. the mixture was shaken with water and dried over P2O5. After addition of 10 cc. anhydrous HCN the mixture was saturated with dried HCl, while cooling with salt and ice. The mixture was chilled overnight to give the imine hydrochloride of the aldehyde, which was hydrolyzed with ice water to give 15 g. II, m. 106° (alc.), also prepared by addition of acrylonitrile to 2,4-dimethyl-3-formyl-5-carbethoxypyrrole; oxime m. 142° (MeOH); N-Ac derivative of the oxime, m. 118° (alc.); semicarbazone m. 210-11°; phenylhydrazone m. 128° (EtOH); azlactone, yellow plates, m. 147° (EtOH).

2,4-Dimethyl-5-carbethoxy-1-pyrrolepropionamide (0.5 g.) in 10 cc. absolute Et2O with 0.3 cc. HCN and HCl gas gave 2,4-dimethyl-3-formyl-5-carbethoxy-1-pyrrolepropionamide, m. 188° (alc.). II (0.5 g.) was stirred with 5 cc. of 7.5% NaOEt in absolute alc., 0.3 cc. hydrazine hydrate was added and heated in pressure tube 10 hrs. at 160-70° to give 2,3,4-trimethylpyrrole, m. 36°; picrate m. 140-2° (alc.). I (0.6 g.) in 1 cc. hot Ac2O was treated with SnCl2.2H2O to give 0.2 g. IV, m. 76° (alc.). 2,4-Dimethyl-3-acetyl-5-carbethoxy-1-pyrrolepropionamide, obtained from 0.6 g. 2,4-dimethyl-5-carbethoxy-1-pyrrolepropionamide with Ac2O by a process analogous to that for preparation of IV, m. 167° (MeOH). IV was also prepared by addition of acrylonitrile to 2,4-dimethyl-3-acetyl-5-carbethoxypyrrole. 2,3-Dimethyl-4-carbethoxy-1-pyrrole-5-carboxaldehyde (1 g.) with acrylonitrile gave 0.9 g. V, yellow needles, m. 114° (alc.). 2,4-Dimethyl-3,5-dicarbethoxypyrrole (1 g.) with acrylonitrile gave 0.8 g. III, m. 106° (alc.). III (0.5 g.) heated with 3 cc. 7.5% NaOEt in absolute alc. in a pressure tube 10 hrs. at 150° gave by recrystn. 2,4-dimethyl-3,5-dicarbethoxypyrrole, m. 132°. VI (0.9 g.) was obtained from 1 g. 2,3-dimethyl-5-carbethoxypyrrole, m. 63° (alc.). 2-Methyl-5-carbethoxypyrrole gave VII, m. 58° (alc.); 2-methyl-3-carbethoxypyrrole gave VIII, m. 93° (alc.). 2,4-Dimethyl-3-ethylpyrrole (5 cc.) gave 3 g. IX, b0.2 130°; picrate m. 185° (alc.). Freshly distilled 2,4-dimethylpyrrole (5 g.) and acrylonitrile gave 3 g. X, yellow oil, b11 149°. A similar reaction gave XI, m. 101°.

2,4-Dimethyl-5-carboxy-1-pyrrolepropionic acid amide (XIV). I (5 g.) in 8 cc. alc. and a solution of 5 g. KOH and 10 cc. water was heated to boiling on water bath, whereby NH3 began to evolve. After some time, also in the heat, the resulting precipitate of K salt was separated, washed, dissolved in H2O, and the solution acidified with dilute AcOH to give 1.2 g. (purified) 2,4-dimethyl-5-carboxy-1-pyrrolepropionamide (XVII), m. 195° (Me2CO); Me ester m. 166° (MeOH). I (5 g.) was heated to boiling for 10 hrs. in 8 cc. alc. and 5 g. KOH in 10 cc. water.

The first separated K salt of XVII redissolved for the greater part. The mixture was filtered, the filtrate cooled to 0° and 2 g. 2,4-dimethyl-5-carboxy-1-pyrrolepropionic acid (XVIII) precipitated by careful acidification with AcOH, 90-100° (decomposition). Decomposition of XVIII by heating gave 2,4-dimethyl-1-ethylpyrrole; picrate not m. below 300°, further heating caused detonation. I (3 g.) in 30 cc. absolute Et2O and 3 cc. absolute alc. was cooled with ice and salt and saturated with anhydrous HCl to give the imide hydrochloride of Et 2,4-dimethyl-5-carbethoxy-1-pyrrolepropionate (XIX). Hydrolysis with ice water gave XIX, oil, b11 178°. I (0.6 g.) was added to 10 cc. of mixture of equal parts of HI (d. 1.70) and glacial AcOH and heated 2 hrs. on the boiling water bath. The dark brown solution was decolorized with granular Ph4I and the solvent was evaporated in a vacuum on the water bath.

NaOAc solution was added to the residue to neutralize the HI. The residue was crystallized to yield 0.4 g. 2,4-dimethyl-5-carbethoxy-1-pyrrolepropionamide (XX) m. 159° (alc.). Saponification with aqueous alc. KOH gave XVII. XIX (1 g.) was added to 10 cc. of a concentrated solution of NH<sub>3</sub> in absolute alc. and allowed to stand closed for 1 week. The solution was evaporated and the residue recrystd. from alc. to give XX. Equal parts of XX and P2O5 heated at 200° in a vacuum gave I. II (1 g.) was dissolved in 10 cc. alc., 0.8 g. malonic acid and 0.7 cc. freshly distilled aniline was added, and the mixture heated 12 hrs. on boiling water bath to give 1.2 g. XII, m. 186° (CHCl<sub>3</sub>). XII was dissolved in 10% NaOH solution and within 6 hrs., with stirring, excess 3% Na-Hg was added. The temperature was held between 12 and 15°, and from time to time enough dilute HCl was added so that turbidity resulted. In this manner the saponification of the carbethoxy residue by the developing alkalinity was avoided. After removal of the mixed greases with Et<sub>2</sub>O the watery layer was cooled to 0°, acidified cautiously with dilute AcOH just to an acid reaction; the precipitate was immediately filtered off and dried on an unglazed plate to yield 70% XIII, pink, m. 133° (alc.). II (1 g.) was dissolved in 4 cc. absolute alc., then 1 cc. MeNO<sub>2</sub> and 0.05 cc. 20% MeNH<sub>2</sub> in absolute alc. was added and the mixture heated to boiling on the water bath to give 0.8 g. gold-yellow XIV, m. 145° (alc.). XIV (3 g.) was finely powdered and slurried in 100 cc. dry Et<sub>2</sub>O and 3 g. Al-Hg was added in several portions with frequent shaking. The reduction was held in process through the repeated addition of several drops of water. It was allowed to stand overnight, filtered and the slime extracted with Et<sub>2</sub>O. The combined exts. were dried with Na<sub>2</sub>SO<sub>4</sub> and the solvent evaporated. The residue was recrystd. from acetone to yield 30 to 40% XV, m. 166°. XV (0.2 g.) was dissolved in 4 cc. Ac<sub>2</sub>O then 0.4 g. anhydrous NaOAc was added and heated 2 hrs. on the boiling water bath; then 25 cc. water was added. After several hrs. XVI separated, m. 90° (alc.). 2-Methyl-3-formyl-5-carbethoxypyrrole (5 g.) was heated 2 hrs. on a boiling water bath in 20 cc. absolute alc. with 3 cc. nitromethane and 0.5 cc. of a 20% solution of methylamine in absolute alc. to give 70% yellow 2-methyl-3-(2-nitrovinyl)-5-carbethoxypyrrole (XXI), m. 195° (alc.). Reduction of XXI with Al-Hg gave 30% 2-methyl-5-carbethoxypyrrole 3-acetaldoxime (XXII), m. 158-61° (alc.). A suspension of 10 g. 2-methyl-5-carbethoxypyrrole in 20 cc. absolute Et<sub>2</sub>O and 20 cc. alc.-free dried CHCl<sub>3</sub> and 8 g. NCCO<sub>2</sub>Et was cooled in ice-salt, saturated with dry HCl, and allowed to stand overnight in the cold to give a quant. yield of the imide-HCl of Et 2-methyl-5-carbethoxy-3-pyrroleglyoxylate (XXIII). The imide hydrochloride stirred in 400 cc. of ice water gave after several hrs. XXIII, m. 160° (alc.); phenylhydrazone, yellow, m. 144° (alc.); hydrazide (XXIV) m. 197°; benzoylhydrazide m. 248°. XXIII (1 g.) with 7 cc. 7.5% NaOEt heated with 0.5 cc. hydrazine hydrate 10 hrs. at 165-70° gave the very labile 2-methylpyrrole-5-carboxylic acid-3-acetic acid which was not isolated, but was treated with CH<sub>2</sub>N<sub>2</sub> in Et<sub>2</sub>O to give 50 mg. Me 2-methyl-5-carbomethoxy-3-pyrroleacetate (XXV), m. 103° (alc.). Et 2-methyl-5-carbethoxy-3-pyrrolepropionate (XXVI), 60% from 5 g. 2-methyl-5-carbethoxy-3-pyrrolepropionic acid in 50 cc. of a saturated solution of HCl in absolute alc., m. 65° (alc.). XXVI (5 g.) heated 2 hrs. on a boiling water bath in 10 cc. alc. with 2 cc. hydrazine hydrate gave a mixture of the hydrochloride of 2-methyl-5-carbethoxy-3-pyrrolepropionic acid hydrazide and N<sub>2</sub>H<sub>4</sub>.HCl. 2-Methyl-5-carbethoxy-3-pyrrolepropionic acid azide. This mixture was dissolved in 10 times the amount of water and filtered from undissolved material. The solution was cooled with ice and an ice cold 10% solution of NaNO<sub>2</sub> in excess was added carefully. The azide precipitated crystalline and was used without purification. The completely dried crude azide was dissolved in 10 times the amount of absolute

alc. and heated to boiling on the water bath; N actively evolved. After 3 hrs. the alc. was evaporated and the urethan recrystd. from absolute alc. to give 0.5 g. Et (2-methyl-5-carbethoxy-3-pyrrol)ethylcarbamate (XXVII), m. 120° (alc.). 2-Methyl-5-carbethoxy-3-pyrrolepropionic acid (1 g.) was heated to boiling in 10 cc. glacial AcOH with 1.4 g. pure, completely dried bromomalonic acid. After 5 min. 10 cc. hot water was added and the solution allowed to cool to give by repeated crystallization from AcOH and water 1 g. brown 4-bromo-2-methyl-5-carbethoxy-3-pyrrolepropionic acid, m. 180° (decomposition). 2,3-Dimethyl-5-carbethoxypyrrole (0.2 g.) in 2 cc. glacial AcOH and 0.3 g. pure and completely dried bromomalonic acid gave from glacial AcOH and water 0.2 g. brown needles of 4-bromo-2,3-dimethyl-5-carbethoxypyrrole, m. 152° (decomposition). 4-Bromo-2,3-dimethyl-5-pyrrolecarboxylic acid azide (0.2 g.) was prepared from 0.2 g. 2,3-dimethyl-5-pyrrolecarboxylic acid azide and 0.3 g. bromomalonic acid, brown needles, m. 145° (decomposition) (glacial AcOH and water).

- CC 10G (Organic Chemistry: Heterocyclic Compounds)  
 IT Rearrangements  
     (of pyrrole-1-propionitrile derivs.)  
 IT Cyanoethylation  
     (of pyrroles)  
 IT 53451-57-3, 2-Selenophenecarboxaldehyde, 5-nitro- 57500-58-0,  
 2-Selenophenecarboxaldehyde, 4-nitro- 103386-46-5, Pyrrole-2-carboxylic  
 acid, 1-(2-carbamoylethyl)-3,5-dimethyl-  
     (and derivs.)  
 IT 2199-44-2, Pyrrole-2-carboxylic acid, 3,5-dimethyl-, ethyl ester  
     (and its cyanoethylation)  
 IT 14306-10-6, Pyrrole-2-carboxylic acid, 3,5-dimethyl-4-(2-nitrovinyl)-,  
 ethyl ester 37789-64-3, Pyrrole-3-propionic acid, 5-carboxy-2,4-dimethyl-  
     , 5-ethyl ester  
     (cyanoethylation of)  
 IT 857201-02-6, Pyrrole-3-glyoxylic acid, 5-carboxy-2-methyl- 857202-10-9,  
 Pyrrole-2-carboxylic acid, 1-(2-carbamoylethyl)-4-formyl-3,5-dimethyl-  
 857204-81-0, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-4-formyl-3,5-  
 dimethyl- 858027-49-3, Pyrrole-3-propionic acid, 5-carboxy-2-methyl-  
     (derivs.)  
 IT 109-97-7, Pyrrole  
     (derivs., cyanoethylation of)  
 IT 1466-76-8, Benzoic acid, 2,6-dimethoxy- 2141-62-0, Propionitrile,  
 3-ethoxy- 2436-79-5, Pyrrole-2,4-dicarboxylic acid, 3,5-dimethyl-,  
 diethyl ester 3855-78-5, Pyrrole, 2,3,4-trimethyl- 53871-28-6,  
 Pyrrole, 1-ethyl-2,4-dimethyl- 98550-56-2, Pyrrole-2-carbonyl azide,  
 3-bromo-4,5-dimethyl- 99069-04-2, Pyrrole-2-carboxylic acid,  
 5-methyl-4-(2-nitrovinyl)-, ethyl ester 99076-49-0, Pyrrole-1-propionic  
 acid, 2-carboxy-3,5-dimethyl- 99362-09-1, Pyrrole-1-propionitrile,  
 2,4-dimethyl- 100057-91-8, Pyrrole-2-carboxylic acid,  
 4-[2-(azidoformyl)ethyl]-5-methyl-, ethyl ester 100129-25-7,  
 Pyrrole-3-propionic acid, 4-bromo-5-carboxy-2-methyl-, 5-ethyl ester  
 100387-91-5, Pyrrole-2-carboxylic acid, 4-bromo-1-(2-cyanoethyl)-3,5-  
 dimethyl-, ethyl ester 100720-06-7, Pyrrole-2-carboxylic acid,  
 1-(2-cyanoethyl)-4-(cyanomethyl)-3,5-dimethyl-, ethyl ester 100720-50-1,  
 Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-3,5-dimethyl-4-(2-nitrovinyl)-  
     , ethyl ester 100723-41-9, Pyrrole-2-carboxylic acid,  
 4-acetyl-1-(2-cyanoethyl)-3,5-dimethyl-, ethyl ester 100797-07-7,  
 Pyrrole, 2,3,4-trimethyl-, picrate 100801-06-7, Pyrrole-2-carboxylic  
 acid, 4-(2-carboxyaminoethyl)-5-methyl-, diethyl ester 100876-64-0,  
 Pyrrole-2-carboxylic acid, 4-acetyl-1-(2-carbamoylethyl)-3,5-dimethyl-,  
 ethyl ester 100958-54-1, Pyrrole-3-acrylic acid, 5-carboxy-1-(2-  
 cyanoethyl)-2,4-dimethyl-, 5-ethyl ester 101117-13-9,



Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-4-(formylmethyl)-3,5-dimethyl-, ethyl ester, oxime 101257-49-2, Pyrrole-3-acetic acid, 5-carboxy-2-methyl- 101496-90-6, Pyrrole-3-propionic acid, 5-carboxy-1-(2-cyanoethyl)-2,4-dimethyl-, 5-ethyl ester 101580-02-3, Pyrrole-1-propionitrile, 3-ethyl-2,4-dimethyl- 101580-03-4, Pyrrole-1-propionitrile, 3-ethyl-2,4-dimethyl-, picrate 101879-23-6, Hydrazine, 1-benzoyl-2-[(5-carboxy-2-methylpyrrol-3-yl)glyoxyloyl]-, ethyl ester 102236-53-3, Pyrrole-2-carboxylic acid, 3-bromo-4,5-dimethyl-, ethyl ester 102459-97-2, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-3,5-dimethyl-4-[(5-oxo-2-phenyl-2-oxazolin-4-ylidene)methyl]-, ethyl ester 103095-40-5, Pyrrole-3-acetic acid, 5-carboxy-2-methyl-, dimethyl ester 103386-48-7, Pyrrole-2-carboxylic acid, 4-(formylmethyl)-5-methyl-, ethyl ester, oxime 103853-68-5, Pyrrole-3-carboxylic acid, 1-(2-cyanoethyl)-2-methyl-, ethyl ester 103855-57-8, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-5-methyl-, ethyl ester 103990-79-0, Pyrrole-2-carboxylic acid, 4-[2-[carboxy(2-cyanoethyl)amino]ethyl]-1-(2-cyanoethyl)-3,5-dimethyl-, diethyl ester 105336-91-2, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-4,5-dimethyl-, ethyl ester 105337-45-9, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-3,5-dimethyl-, ethyl ester 107418-00-8, Pyrrole-2,4-dicarboxylic acid, 1-(2-cyanoethyl)-3,5-dimethyl-, diethyl ester 107682-89-3, Pyrrole, 1-ethyl-2,4-dimethyl-, picrate 108482-19-5, Pyrrole-3-acetic acid, 5-carboxy- $\alpha$ -imino-2-methyl-, diethyl ester, hydrochloride 108953-98-6, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-4-formimidoyl-3,5-dimethyl-, ethyl ester, hydrochloride 109366-54-3, Pyrrole-2-carboxylic acid, 1-[2-(1-ethoxyformimidoyl)ethyl]-3,5-dimethyl-, ethyl ester, hydrochloride 109366-54-3, Pyrrole-1-propionimidic acid, 2-carboxy-3,5-dimethyl-, diethyl ester, hydrochloride 109394-74-3, Pyrrole-1-propionic acid, 2-carboxy-3,5-dimethyl-, diethyl ester 113324-72-4, Pyrrole-3-carboxylic acid, 1-(2-cyanoethyl)-2-formyl-4,5-dimethyl-, ethyl ester (preparation of)

IT 107-13-1, Acrylonitrile  
(reaction of, with pyrrole derivs.)  
IT 107-13-1, Acrylonitrile  
(reaction of, with pyrrole derivs.)  
RN 107-13-1 HCAPLUS  
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



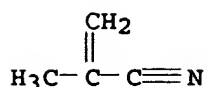
L36 ANSWER 34 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN  
AN 1959:56231 HCAPLUS  
DN 53:56231  
OREF 53:10111c-i,10112a-i,10113a-c  
TI Pyrolysis. XIII. Competitive alkyl-O and acyl-O scission in the pyrolysis of esters;  $\alpha,\alpha$ -disubstituted cyanomethyl carboxylates  
AU Bennett, R. N.; Deans, A. A.; Harris, J. G. H.; Ritchie, P. D.; Shim, J. S.  
CS Roy. Coll. Sci. Technol., Glasgow, UK  
SO Journal of the Chemical Society, Abstracts (1958) 4508-15  
CODEN: JCSAAZ; ISSN: 0590-9791  
DT Journal  
LA Unavailable  
AB cf. C.A. 52, 9973c. New evidence, coupled with a survey of the literature, shows that the well-known alkyl-oxygen scission of carboxylic esters to carboxylic acid plus alkene (vapor phase, about

400-500°) occurs in competition with a less familiar acyl-O scission by what is essentially a retro-Tishehenko reaction. The molar ratio of these 2 primary routes can vary over a wide range, with alkyl-O and acyl-O scission as the extreme limiting cases. Factors governing the balance between them are discussed, and the occurrence of further reactions is briefly noted. To show that a primary competition between alkyl-O and acyl-O scission exists, with subsequent secondary breakdown of some of the primary products, and to test the general validity of the concept, six 1-cyanoalkyl and 1-cyanocycloalkyl esters were studied. These were: BzOCMe<sub>2</sub>CN (I), BzOCMeEtCN (II), AcOC-MeEtCN (III), X(OBz)CN (X = cyclopentylidene) (IV), X(OBz)CN (X = cyclohexylidene) (V), and X(OBz)CN (X = cycloheptylidene) (VI). The results fully confirm the idea of competition between the 2 scissions where both are structurally permissible. All 6 esters, which each contain at least one β-H atom, undergo a major A' scission (90%) with a competing minor B2 scission (up to 10%). At high temps. used (500°), acyl cyanide from the B2 reaction is too unstable to survive in the pyrolyzate, but in each case its known breakdown products are observed, sometimes together with further minor secondary products. Three different flow-vessels were used, P 1, P 2 (borosilicate glass), and S (stainless steel). All were packed with borosilicate glass tubing, the free unpacked space being 125, 50, and 80 ml., resp. Two tables summarized the general conditions and results from 14 runs. Apparent losses in weight are due to carbonization and (or) holdup in the packed vessel. The examination of typical pyrolyzates is given below. HCN was removed from exit gases by a cold trap, and ketene by a PhNH<sub>2</sub>-Et<sub>2</sub>O trap. Aldehydes and ketones are characterized by their 2,4-dinitrophenylhydrazones, benzene as m-dinitrobenzene, and PhCN by conversion to benzamide. I is obtained in 42% yield as an oil, b<sub>70</sub> 184-5°, solidifying to crystals, m. 36°. The following data are obtained (compound pyrolyzed, run number, reaction vessel, temperature, feed rate in g./min., contact time in sec., weight of pyrolyzed g., g. in main receiver, l. of gaseous pyrolyzate, % composition of CO, CO<sub>2</sub>, unsatd. hydrocarbons, composition of total pyrolyzate BzOH, olefinic nitrile, ketone, benzonitrile, C<sub>6</sub>H<sub>6</sub>, unchanged pyrolyzant, HCN, and processing losses, tars, gases, etc., given): I, 1, S, 400°, 1.46, 11, 90.7, 82.4, 5.6, 11, 89, nil, present (p), (p), (p), (p), (p), -, -, -; II, 2, S, 510°, 1.25, 12, 100.0, -, 0.5, (p), (p), -, (p), (p), (p), (p), -, -, -, -; IV, 10, P 2, 495°, 0.60, 17, 69.0, 67.2, 1.5, 25, 75, nil, 32.0, 22.5, 1.2, 1.8, 3.0, nil, (0.7), 8.5; V, 11, P 2, 395°, 0.60, 21, 63.0, 61.0, -, -, -, -, 17.6, 14.7, 8.7, 9.7, nil, 2.8, (0.1), 9.5; V, 12, P 2, 495°, 0.80, 16, 76.0, 71, 4.0, 11, 88, 1, 31.0, 25.5, 2.0, 1.8, 0.8, nil, (0.1), 14.9; V, 13, P 2, 555°, 0.50, 20, 49.0, 47.2, -, -, -, -, 20.3, 18.2, 0.8, 0.7, 0.4, nil, (0.2), 8.6; VI, 14, P 2, 495°, 0.43, 27, 64.0, 63.0, 1.2, 26, 74, nil, 17.7, 18.0, 8.6, 7.5, 0.3, nil, (0.3), 11.9. For III the following results were obtained (run number, reaction vessel, temperature, feed rate g./min., contact time in sec., weight pyrolyzed in g., (a) g. in main receiver, (b) gaseous products, % composition of (b) CO, CO<sub>2</sub>, unsatd. hydrocarbons, saturated hydrocarbons, composition of total pyrolyzate in g. AcOH by titration, by fractionation, b. 112-16° total, nitrile, b. 117-19° total, nitriles, b. 120-4°, total, nitrile, b. below 92° mostly MeCOEt, unchanged pyrolyzant, HCN given): 3, P 1, 425°, 2.0, 9, 100.0, 99.9, 2.9, -, -, -, -, 40.7, 38.1, 23.0, 20.2, 6.8, 6.5, 11.6, 10.4, 4.2, 3.0, 0.01; 4, P 1, 425°, 3.3, 6, 100.0, 99.7, 2.2, 38, 2, nil, 60, 41.2, 37.9, 10.2, 8.6, 11.9, 11.6, 18.3, 16.5, 3.1, 1.5, trace; 5, P 1, 425°, 9.7, 2, 100.0, 99.6, 2.0, 31, nil, nil, 69, 37.5, 42.1, 16.8, 14.4, 2.8, 1.7, 17.7, 16.0, 3.2, 9.5, trace; 6, P. 1, 475°, 2.5, 2.5, 7, 100.0, 88.5, -, -, -, -, -, 40.3, 26.2, 24.0, nil, nil, 8.2, 7.6, 0.2, 3.0, 0.02; 7, P 1, 475°, 4.4, 4, 100.0, 95.2, 1.4, 65, 6, 4, 25, -, 38.5, 24.1, 20.8, nil, nil, 5.7, 5.5, 0.2,

1.0, 0.01; 8, P 1, 475°, 10.9, 2, 100.0, 98.5, 2.6, 52, 1, 2, 45, 39.0, 40.5, 16.3, 12.3, 12.5, 11.7, 8.1, 6.2, 2.4, 4.0, 0.01; 9, P 1, 525°, 4.4, 4, 100.0, 91.6, 2.7, 51, 12, 7, 30, 39.9, 39.3, 11.6, 10.0, 2.1, 1.2, 15.6, 15.1, 3.8, 1.0, 0.01. Run 1. No HCN could be detected. Distillation of (a) gave a trace of Me<sub>2</sub>CO, 44 g. substance, b. 70-95°, and a solid residue. The 44 g. fraction gave C<sub>6</sub>H<sub>6</sub>, α-methylacrylonitrile, b. 91-1.5°, and the residue yielded 30 g. BzOH and 2 g. benzonitrile, b. 68-72°. Equimolar quantities of MeCOEt, BzCl, and KCN treated as for I, the final reaction mixture extracted with Et<sub>2</sub>O, the extract washed with Na<sub>2</sub>CO<sub>3</sub>, dried, and distilled gave 40% II, b. 151-75-80°. Alternatively equimolar amts. of redistd. MeCOEt cyanohydrin, BzCl, and tech. C<sub>5</sub>H<sub>5</sub>N heated 1 hr. at 100° cooled, the solid C<sub>5</sub>H<sub>5</sub>N.HCl separated by decantation of the liquid, the liquid washed, and distilled gave 35% II. Run 2. The pyrolysis of II was not studied in full detail, but sufficient evidence was obtained to demonstrate qualitatively the competition between A1 and B2 scissions. Distillation of (a) gave a trace of MeCOEt, a main liquid fraction, b. 110-30°, which embraced the b.p. of CH<sub>2</sub>:C(Et)CN (VII) and MeCH:CMcCN (VII) (VII, b. 114°, VIII, b. 122°); this fraction was unsatd. and evolved NH<sub>3</sub> when heated with alkali, all confirming the presence of olefinic nitriles. EtCOMe cyanohydrin and Ac<sub>2</sub>O warmed with a trace of concentrated H<sub>2</sub>SO<sub>4</sub> and the cooled mixture shaken with brine, and the non-aqueous layer distilled gave 68% pure III, b. 13 92-4°, b. 198-9°. Runs 3-9. These runs gave qualitatively similar results. In each run, the products were worked up in 4 stages. The liquid (a) was distilled, the 1st volatile fraction was added to the liquid in the cold trap, and the HCN determined. The presence of ketene was shown by the detection of acetanilide in the PhNH<sub>2</sub> trap. The total free AcOH determined by titrating with a control experiment showed that olefinic nitriles did not interfere. The bulk of the AcOH was removed by shaking with brine and the insol. layer dried and fractionally distilled; the plot of the cumulative distillative volume against b.p. showed a plateau at 80°: fractions contained MeCOEt, VII, and VIII. The nitrile content was measured via the N content of those fractions. IV obtained in 65% yield as prisms, m. 51-2°. Pyrolysis 10. Distillation of (a) gave: 3.3 g., b. 70-96° consisting of C<sub>6</sub>H<sub>6</sub> and cyclopentanone (IX); 0.8 g., b. 130-2°, containing IX; 23 g., b. 164-70°, yielded 78% 1-cyanocyclopentene which on alkaline hydrolysis gave 86% 1-cyclopentenecarboxylic acid; 1.6 g., b. 170-98°, and 36 g. residue which yielded 6% PhCN, and 84% BzOH. There was no unchanged IV. The alkaline trap contained 0.7% HCN. V was obtained in 70% yield as prisms, m. 73-4°. Pyrolyses 11-13. These runs gave similar results. Run 12 is typical. Distillation of (a) gave: 0.8 g., b. 80°, containing C<sub>6</sub>H<sub>6</sub>; 27 g., b. 84-170°, which redistd. gave 2 g., b. 156-7°, of cyclohexanone; 33 g., b. 170-220° which when redistd. gave 1.8 g., b. 190-5°, mainly PhCN and 25.5 g., b. 195-8° mainly 1-cyanocyclohexene; 27 g., b. 144-8°, BzOH; and 4.5 g. residual tar. The alkali trap contained about 0.1% HCN. VI, prepared in 20% yield in the same lines as IV and V as prisms, m. 72.5° (MeOH). Several variations failed to give yields comparable with those of IV and V. Pyrolysis 14. Distillation of (a) gave 0.3 g., b. about 80°, C<sub>6</sub>H<sub>6</sub>; 41 g., b. 176-225°, redistn. gave 20.9 g. containing cycloheptanone and PhCN, careful fractionation gave 8.6 g., b. 180-2°, mostly cycloheptanone and 7.5 g., b. 192-4° mostly PhCN, this fraction also gave about 58% 1-cyanocycloheptene, b. 213-14° converted by alkaline hydrolysis into 1-cycloheptenecarboxylic acid; 16.5 g., b. 118-20°, mostly BzOH, and 3 g. residual tar. There was no unchanged VI. The alkaline trap contained 0.3% HCN. Freshly redistd. com. CN<sub>2</sub>:CHCN was used, b.

78-9°. Pyrolysis 15. Preliminary runs in vessel P 2 showed the nitrile was very thermostable at 500-600°. At 650°, 20 g. of the nitrile gave 17.3 g. unchanged material plus 2.0 g. high boiling tars; an alkali trap removed 0.2% HCN and displaced N plus a little CH.tplbond.CH. A carboxylic ester may in principle follow at least 2 distinct thermal breakdown routes, A1 and B2, the balance being dictated by the presence or absence of some critical structural feature. The number and type of  $\alpha$ -substituents in a Me ester have a critical bearing on the result. The reaction temperature itself influences the A1-B2 ratio. Although IV, V, and VI cannot yield HCN by the same route as does III, they did produce a slight trace of it on pyrolysis. Its origin is uncertain. A control experiment shows that CH<sub>2</sub>:CHCN does break down on pyrolysis but is not thermostable and the yield of HCN was only 0.2% at 650°. In the above cases the  $\alpha$ -C atom of the alkyl group is fully substituted. When this is not so and the  $\alpha$ -C atoms bear at least one H atom, simple competition between A1 and B2 scissions may be complicated by the appearance of 2 other concurrent competitive reactions. One of these will be described elsewhere.

CC 10E (Organic Chemistry: Benzene Derivatives)  
 IT Bonds  
     (carbon-O, breaking of, in esters)  
 IT Polyesters  
     (decomposition by heat)  
 IT 4111-08-4, Butyronitrile, 2-hydroxy-2-methyl-  
     (esters, preparation and pyrolysis of)  
 IT 126-98-7, Methacrylonitrile  
     (formation in cyanoalkyl ester pyrolysis)  
 IT 502-42-1, Cycloheptanone  
     (formation in pyrolysis of 1-cyanocycloheptyl benzoate)  
 IT 1647-11-6, Butyronitrile, 2-methylene- 20068-02-4, Angelonitrile  
     (formation in pyrolysis of cyanoalkyl esters)  
 IT 74-90-8, Hydrocyanic acid  
     (formation of, in cyanoalkyl ester decompose by heat)  
 IT 65-85-0, Benzoic acid 67-64-1, Acetone 71-43-2, Benzene 463-51-4,  
     Ketene  
     (formation of, in cyanoalkyl ester pyrolysis)  
 IT 108-94-1, Cyclohexanone  
     (formation of, in pyrolysis of 1-cyanocyclohexyl benzoate)  
 IT 120-92-3, Cyclopentanone  
     (formation of, in pyrolysis of 1-cyanocyclopentyl benzoate)  
 IT 64-19-7, Acetic acid 78-93-3, 2-Butanone 100-47-0, Benzonitrile  
     (formation of, in pyrolysis of cyanoalkyl esters)  
 IT 32379-40-1, Cyclohexanecarbonitrile, 1-hydroxy-, benzoate 32379-42-3,  
     Lactonitrile, 2-methyl-, benzoate 32379-43-4, Cyclopentanecarbonitrile,  
     1-hydroxy-, benzoate 106950-67-8, Cycloheptanecarbonitrile, 1-hydroxy-,  
     benzoate  
     (preparation and pyrolysis of)  
 IT 636-82-8, 1-Cyclohexene-1-carboxylic acid 1560-11-8,  
     1-Cyclopentene-1-carboxylic acid 1855-63-6, 1-Cyclohexene-1-carbonitrile  
     3047-38-9, 1-Cyclopentene-1-carbonitrile 4321-25-9, 1-Cycloheptene-1-  
     carboxylic acid 20343-19-5, 1-Cycloheptene-1-carbonitrile  
     (preparation of)  
 IT 126-98-7, Methacrylonitrile  
     (formation in cyanoalkyl ester pyrolysis)  
 RN 126-98-7 HCAPLUS  
 CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



L36 ANSWER 35 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1958:97720 HCAPLUS

DN 52:97720

OREF 52:17170a-h

TI Aromatization of the Diels-Alder adduct of tetraphenylcyclopentadienone and fumaronitrile

AU Doering, Robert F.; Miner, Robert S., Jr.; Rothman, Leonard; Becker, Ernest I.

CS Polytech. Inst. of Brooklyn, Brooklyn, NY

SO Journal of Organic Chemistry (1958), 23, 520-2

CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA Unavailable

AB Reaction of tetraphenylcyclopentadienone (I) and fumaronitrile (II) in PhBr gave trans-1,2-dihydrotetraphenyl-o-phthalonitrile (III). Br converted III to tetraphenyl-o-phthalonitrile (IV). Alkali dehydrocyanated III to 2,3,4,5-tetraphenylbenzonitrile (V). I (12 g.) and 2.8 g. II in 12 ml. PhBr refluxed 5.25 hrs., cooled to room temperature, and crystallized gave 10.09 g. III, m. 230-32° (C<sub>6</sub>H<sub>6</sub>) (gas evolved during melting). I and II directly formed IV without isolation of III (procedure A) or from III (procedure B). Procedure A. II (8.5 g.) and 38.4 g. I in 75 ml. PhBr refluxed until the effluent gases would no longer reduce a 0.02% solution of PdCl<sub>2</sub> (about 2 hrs.), the mixture cooled, treated with 24 g. Br in 25 ml. PhBr, and refluxed 3 hrs. gave 13.4 g. IV, m. 265.3-5.4° (C<sub>6</sub>H<sub>6</sub>). Procedure B. A refluxing solution of 0.10 g. III in 2 ml. PhBr treated dropwise with 0.156 g. Br in 2 ml. PhBr, the mixture refluxed 3.5 hrs., the solution distilled to dryness, and the residue extracted with ligroine gave 0.050 g. IV. IV (1 g.) refluxed 12 hrs. with an excess of 10% alc. KOH gave tetraphenyl-o-phthalic anhydride, m. 289-90° (C<sub>6</sub>H<sub>6</sub>). I and CH<sub>2</sub>:CHCN refluxed in C<sub>6</sub>H<sub>6</sub> or alone gave 7-oxo-1,4,5,6-tetraphenylbicyclo[2.2.1]hept-5-ene-2-carbonitrile (VI). I (1 g.) in 2.4 g. CH<sub>2</sub>:CHCN kept 4.5 hrs. during which time the red-purple color was discharged and cooled gave 0.63 g. VI, m. 204-6° (decomposition). VI (0.5 g.) in 3 ml. PhBr slowly heated to reflux (the color changed and there was no evidence of gas evolution), the mixture refluxed 5 hrs. with 3 ml. CH<sub>2</sub>:CHCN (the purple color discharged), and distilled gave 96% unchanged VI. VI on decarboxylation in either PhNO<sub>2</sub> or in p-cymene gave similar results. The use of PhNO<sub>2</sub> is described. Crude VI (2 g.) and 5 ml. CH<sub>2</sub>:CHCN in 90 ml. PhNO<sub>2</sub> refluxed 10 hrs. at 165° gave 0.78 g. 2,3-dihydro-3,4,5,6-tetraphenylbenzonitrile (VII), m. 192.5-4.0° (C<sub>6</sub>H<sub>6</sub>-ligroine). VII (0.56 g.) and 0.4 g. Br in 30 ml. PhBr refluxed 6 hrs., the solvent distilled, and the residue recrystd. gave 0.49 g. V, m. 216-17° (alc.). A C<sub>6</sub>H<sub>6</sub> solution of 0.197 g. III passed through a column of Merck Al<sub>2</sub>O<sub>3</sub> gave 88% V. III heated 15 min. at 240-50° with gas evolution and cooled gave a poor yield of V. I (1.02 g.) and 0.0109 g. diethylenetriamine in 10 ml. PhBr refluxed 1 hr., the evolution of HBr detected by formation of a copious precipitate of AgBr, the solvent removed in vacuo, and the residue crystallized gave 0.95 g. V. All samples of V prepared above were identical. Tetracyclone (3 g.) and 1.48 g. propiolic acid in 10 ml. PhBr slowly heated, the color discharged within 10 min., and before 100° was reached, the solution refluxed 8 hrs., and the solvent removed gave 3.1 g.

2,3,4,5-tetraphenylbenzoic acid (VIII), m. 327.5-8.5° (Me<sub>2</sub>CO). V (0.38 g.), 1 g. KOH, 10 ml. alc., and 0.4 ml. H<sub>2</sub>O refluxed 12.25 hrs., the mixture digested 24 hrs. with 50 ml. more H<sub>2</sub>O on the steam bath, cooled, 10 ml. concentrated HCl added, and the mixture digested 4 hrs. gave 0.36 g. VIII. The yield of pure VIII was very low, however, and digesting 7 hrs. on the steam bath in 20 ml. alc. and 20 ml. 6N H<sub>2</sub>SO<sub>4</sub> did not improve the purity. V (0.27 g.), 4.5 g. concentrated H<sub>2</sub>SO<sub>4</sub>, and 3.3 ml. H<sub>2</sub>O refluxed 12.25 hrs., diluted, filtered, washed, and recrystd. gave 5% VIII. Infrared spectra were superimposable.

- CC 10E (Organic Chemistry: Benzene Derivatives)  
 IT Dehydrogenation  
     (of tetraphenylcyclohexadienecarbonitriles)  
 IT Diels-Alder reaction  
     (of tetraphenylcyclopentadienone, with acrylonitrile and fumaronitrile)  
 IT 107-13-1, Acrylonitrile 764-42-1, Fumaronitrile  
     (Diels-Alder reaction with tetraphenylcyclopentadienone)  
 IT 103327-38-4, 1,3-Cyclohexadiene-1-carbonitrile, 2,3,4,5-tetraphenyl-  
     (preparation and dehydrogenation of)  
 IT 1181-03-9, Phthalonitrile, tetraphenyl- 3008-21-7, 5-Norbornene-2-  
     carbonitrile, 7-oxo-1,4,5,6-tetraphenyl- 52316-18-4, Benzoic acid,  
     2,3,4,5-tetraphenyl- 78672-82-9, Benzonitrile, 2,3,4,5-tetraphenyl-  
     103266-79-1, 3,5-Cyclohexadiene-1,2-dicarbonitrile, 3,4,5,6-tetraphenyl-  
     (preparation of)  
 IT 479-33-4, Cyclopentadienone, tetraphenyl-  
     (reaction (Diels-Alder) with acrylonitrile and fumaronitrile)  
 IT 74-90-8, Hydrocyanic acid  
     (removal of, from 3,4,5,6-tetraphenyl-3,5-cyclohexadiene-1,2-  
     dicarbonitrile)  
 IT 107-13-1, Acrylonitrile  
     (Diels-Alder reaction with tetraphenylcyclopentadienone)  
 RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



- L36 ANSWER 36 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN  
 AN 1953:58498 HCAPLUS  
 DN 47:58498  
 OREF 47:9905i,9906a-i,9907a-i,9908a-b  
 TI Acrylonitrile as a starting material for synthesis of amino nitriles and  
     polyamines  
 AU Kost, A. N.  
 SO Uchenye Zapiski Moskov. Gosudarst. Univ. im. M. V. Lomonosova (1950), (No.  
     131), 39-97  
 DT Journal  
 LA Unavailable  
 AB cf. C.A. 41, 1609h; 42, 3722g. Dissertation at the University (1946) with  
     complete exptl. details and bibliography of 169 references. A laboratory preparation  
     of CH<sub>2</sub>:CHCN (I) was developed as follows. To a hot saturated solution of 100 g.  
     SnCl<sub>2</sub> was added 30 g. Zn dust with stirring and, after completion of  
     reaction, the mixture was allowed to stand 2 hrs., decanted, washed with 10%  
     AcOH, let stand overnight with 60 ml. 80-90% AcOH, filtered, washed with  
     H<sub>2</sub>O until neutral, and washed with EtOH and Et<sub>2</sub>O, giving 30-35 g.  
     Sn dust. All traces of Zn must be removed for good results with this  
     catalyst. Heating 50 g. HOCH<sub>2</sub>CH<sub>2</sub>CN with 5 g. of the above Sn dust in a  
     distillation apparatus with chilled receiver so that vapor temperature is  
     below 110° yields a 2-layer distillate; the upper layer

after drying with  $\text{CaCl}_2$  yields up to 90% I. If com. ethylene oxide is used in the preparation of the cyanohydrin, the product may be contaminated with  $\text{MeCH:CHCN}$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$ ; it is purified by 5-10 min. treatment with  $\text{P}_2\text{O}_5$  and distillation (b758 78°). Refluxing the cyanohydrin with silica gel, activated C,  $\text{MgSO}_4$ , Fe oxides, pieces of sheet Fe, Al foil, and  $\text{Al}_2\text{O}_3$  gave but 0-30% yields of I. Passage of the cyanohydrin over  $\text{Al}_2\text{O}_3$  at 200-20° gave but 18-20% I. To 950 ml. aqueous  $\text{NH}_4\text{OH}$  (saturated in the cold) was added 95 g. I dropwise with cooling over 2 hrs. so that the mixture remained homogeneous; after 30 min. at room temperature, distillation gave 30%  $\text{H}_2\text{NCH}_2\text{CH}_2\text{CN}$ , b14 77-8°, b23 89°, nD20 1.4390, d20 0.9584, which polymerized in several days in a sealed ampul even in darkness. Distillation of the higher-boiling residue gave 47%  $\text{HN}(\text{CH}_2\text{CH}_2\text{CN})_2$ , b14 177-9°, b22 209-11°, nD20 1.4630, d20 1.0196; HCl salt, m. 147-8° (from MeOH); N-Bz derivative, m. 112° (from MeOH). The free amine generated by addition of 50% aqueous  $\text{Me}_2\text{NH}$  to solid NaOH was fed into 106 g. I with ice cooling over 6-8 hrs., and the mixture distilled after 2 hrs. at room temperature yielding 80-1%  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{CN}$ , b750 171°, nD20 1.4283, d20 0.8705; picrate, m. 151°; HCl salt, m. 199° (from MeOH). A mixture of 40 g.  $\text{Et}_2\text{NH}$  and 26.5 g. I gave a slight heat evolution after 5-10 min.; refluxed on a steam bath 2 hrs. (yellow color) and distilled, it yielded 89-95%  $\text{Et}_2\text{NCH}_2\text{CH}_2\text{CN}$ , b20 86-9°. If the heating is done in sealed tubes 6-8 hrs. no yellow color is formed and the yield is nearly 100%; the pure product b2 65°, b9 76°, b20 87°, b45 112°, b755 197.3° (corr.), d20 0.8761, nD20 1.4380; HCl salt, m. 120°; picrate, m. 95°. This (3.1 g.) refluxed 4 hrs. with 4. g. 25% NaOH and evaporated gave the amorphous Na salt of the corresponding acid; refluxing 6.3 g. of the nitrile with 11 g. concentrated HCl, cooling, filtering, and evaporating repeatedly in vacuo gave an amorphous mass, which was freed in aqueous solution of Cl ion by  $\text{Ag}_2\text{CO}_3$ , the Ag ion removed with  $\text{H}_2\text{S}$ , and the filtrate evaporated, yielding 60%  $\text{Et}_2\text{NCH}_2\text{CH}_2\text{CO}_2\text{H}$ , m. 70-5°. The best reaction conditions for piperidine and I are as follows: Piperidine (17 g.) and 11.1 g. I mixed with cooling in an ampul (cooled until the heat evolution stopped in 15-20 min.) and heated 4 hrs. on a steam bath, then let stand overnight, gave 96-7%  $(\text{CH}_2)_5\text{NCH}_2\text{CH}_2\text{CN}$ , b18 114-15°; some 22% is formed by refluxing 5 g. piperidine with 5 g.  $\text{HOCH}_2\text{CH}_2\text{CN}$  3 hrs. at 120-50°; if Sn dust is added the yield is 52.5%. An extensive study showed that the reaction of I with  $\text{PhNH}_2$  is best carried out by heating in an ampul 100 hrs. on steam bath in the presence of 3%  $\text{Ac}_2\text{O}$  and a little hydroquinone, when 65-70%  $\text{PhEtNCH}_2\text{CH}_2\text{CN}$ , b8 158°, b11 164-5°, nD20 1.5503, d20 1.0260, is obtained; HCl salt, hygroscopic solid; picrate, oil; the free base couples with diazotized sulfanilic acid even in acid medium and the coupling product, isolated as the Na salt, is a green solid, giving a brown color in acid solution. Coupling with diazotized p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> gave a brown product, C<sub>17</sub>H<sub>17</sub>O<sub>2</sub>N<sub>5</sub>, while tetrazotized benzidine reacts only slowly in acidified solution, yielding a red-violet solution which turns yellow in neutral or basic solution; the free azo derivative is soluble in organic solvents. Hydrolysis of  $\text{PhEtNCH}_2\text{CH}_2\text{CN}$  is very slow with  $\text{H}_2\text{O}$  at 100° in a sealed tube; concentrated HCl at room temperature acts slowly and incompletely even in 48 hrs., while heating at 110-20° leads to loss of  $\text{PhNH}_2$ ; heating with 30-40%  $\text{H}_2\text{SO}_4$  gives an impure product. Alkaline hydrolysis gives low yields of the corresponding acid. Refluxing 14 g.  $\text{PhEtNCH}_2\text{CH}_2\text{CN}$  and 20 g. KOH in 20 ml.  $\text{H}_2\text{O}$  and 70 ml. EtOH 15 hrs., acidifying with HCl, and repeatedly extracting with iso-BuOH, adding Et<sub>2</sub>O to the extract gave 33.1%  $\text{PhEtNCH}_2\text{CO}_2\text{H} \cdot \text{HCl}$ , a high-melting solid, giving a brown color with  $\text{FeCl}_3$ . This couples even in acid solution with diazotized sulfanilic acid, yielding a red azo derivative; p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>Cl also couples in acid medium, giving a red azo derivative  $\text{PhEtNCH}_2\text{CH}_2\text{CN}$  (4.5 g.) added slowly to 15 ml. concentrated  $\text{H}_2\text{SO}_4$ , and

the mixture let stand 40 hrs., then diluted with H<sub>2</sub>O (50 ml.), neutralized with concentrated NH<sub>4</sub>OH, and let stand overnight giving a precipitate of PhEtNCH<sub>2</sub>CH<sub>2</sub>CONH<sub>2</sub>, 68.5-76.5%, m. 55-8° (crude), m. 67° (from MeOH). I (35 g.) added to 20 g. dry (CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub> dropwise with cooling at 15-20° over 2 hrs. the mixture shaken 2 hrs. at room temperature and let stand overnight in a stoppered flask gave 39.8% H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>CN, b1.5 101°, nD<sub>20</sub> 1.4727, d<sub>20</sub> 0.9912 (with MeZnI at room temperature only the primary amino group reacts, while at 100° all active H can be determined) (the picrate and styphnate are oils, while HCl salt is a viscous mass), and 59.8% (CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>CN)<sub>2</sub>, b1.5 174°, b3.5 191°, nD<sub>20</sub> 1.4793, d<sub>20</sub> 1.0256 [picrate and styphnate, oils; HCl salt, m. 184-7° (decomposition)]. The structure of the latter appears confirmed by the improbability of reaction of I with a cyanoethylated group, and further by the reaction with MeZnI which indicates 1.94 active H atoms/mole at 100° and 0.5 at room temperature Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CN treated with MeI in C<sub>6</sub>H<sub>6</sub> with cooling gave the methiodide, m. 153° (from MeOH); EtI at room temperature yielded the ethiodide, m. 128.5° (from MeOH); EtBr at 60° yielded the ethobromide, m. 157° (from Et<sub>2</sub>O-MeOH); PrBr and CH<sub>2</sub>:CHCH<sub>2</sub>Cl at 80° yielded the corresponding quaternary salts, m. 189° (from Et<sub>2</sub>O-MeOH), and 185-7° (from MeOH), resp. Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CN with MeI at room temperature gave the methiodide, m. 152° (from MeOH), while EtI at 60° gave the ethiodide, m. 168° (from MeOH). (CH<sub>2</sub>)<sub>5</sub>NCH<sub>2</sub>CH<sub>2</sub>CN with MeI at 100° gave the methiodide, m. 152° (from MeOH), while EtI reacted slowly at 100° yielding the ethiodide, m. 160-1° (from MeOH). Reduction of H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CN with BuOH-Na gave variable yields when com. Na was used, because of traces of K (Dzirkal, C.A. 36, 2255.6); a 2% K-Na alloy gave high yields comparable to those obtained with pure Na. In the best procedure 30 g. of this alloy was rapidly treated with 14 g. H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CN in 450 ml. BuOH, and despite vigorous reaction the mixture was immediately heated in an oil bath at 140-50°, cooled after 35-40 min., diluted with 130-50 ml. cold H<sub>2</sub>O, steam-distilled 4-6 hrs. into the calculated amount of aqueous HCl, and the distillate evaporated, yielding 81% CH<sub>2</sub>(CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>.2HCl, m. 242° (from EtOH). Similar reduction of Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CN gave 52-6% Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, b128-30 70-80° (crude), b20 44-5°, b748 133°, nD<sub>20</sub> 1.4415, d<sub>20</sub> 0.8272; di-HCl salt, m. 184° (from MeOH); picrate, C<sub>17</sub>H<sub>20</sub>N<sub>8</sub>O<sub>14</sub>, m. 211° (from H<sub>2</sub>O). The higher-boiling material yielded a little 3,3'-bis(dimethylamino)dipropylamine, b20 128-31°, nD<sub>20</sub> 1.4531 (HCl salt, hygroscopic solid; tripicrate, m. 200°; chloroplatinate, 2C<sub>10</sub>H<sub>25</sub>N<sub>3</sub>.3H<sub>2</sub>PtCl<sub>6</sub>, soluble in H<sub>2</sub>O, insol. in aqueous EtOH). Reduction of Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CN with NaBuOH gave 38-63% diamine; a 2% K-Na alloy gave good consistent 60-70% yields; pure Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, b12 61-2°, b70 85-7°, b80 99-100°, b755 168-70°, nD<sub>20</sub> 1.4435, gave 2 active H with MeZnI at room temperature and at 100°; picrate, m. 190.5° (from MeOH); Bz derivative, oil. Refluxing this amine with an equimolar amount of oleic acid 2 hrs., adding a little amine, heating another hr., concentrating, and evaporating with C<sub>6</sub>H<sub>6</sub> gave a product that formed extremely stable organic-aqueous emulsions. The higher-boiling fractions from the above reduction gave a little bis(diethylamino) dipropylamine, b12 148-50° (picrate, m. 152°), also obtained if the reduction is run with pure Na. Reduction of (CH<sub>2</sub>)<sub>5</sub>NCH<sub>2</sub>CH<sub>2</sub>CN with 2% K-Na in BuOH gave 57% 1-(3-aminopropyl)piperidine, b4 65-6°, b9 79-81°, nD<sub>20</sub> 1.4729. COCl<sub>2</sub> with ROH gave the ClCO<sub>2</sub>R: R =Et, b752 92-4°; Pr, b742 114-16°, nD<sub>20</sub> 1.4036; iso-Pr, b745 101-2°, nD<sub>20</sub> 1.3996, d<sub>20</sub> 1.0777; Bu, b16 40-7°, b756 138°, nD<sub>20</sub> 1.4128, d<sub>20</sub> 1.0513. COCl<sub>2</sub> with ROH in MePh in the presence of 5-8% quinoline gave the following ClCO<sub>2</sub>R: iso-Bu, b750 123-7°; iso-Am, b754 150-1°, nD<sub>20</sub> 1.4176, d<sub>20</sub> 1.0490; C<sub>8</sub>H<sub>17</sub>, b5 86.5°, b10 96-7°, b15



107°, nD20 1.4330, d20 0.9841; cyclohexyl, b25 80-5°, nD25 1.4628; 1-menthyl, b5 96°, b11 108-9°, nD20 1.4712; PhCH2, b7 85-7°; with an equimolar amount of quinoline were obtained: sec-Bu, 72%, b23 30-1°, b748 121-4°, nD20 1.4490; 1-methyl-2-cyclohexyl, b30 101.5°, nD20 1.4560; Ph, b7 64°, nD20 1.5162. The diamines (0.025 mole) in Et2O were treated with 0.025 mole powdered potash, then 1.5-2 ml. H2O, and RO2CCl in Et2O was added with cooling; the usual treatment gave the desired urethan derivs.: Me2NCH2CH2CH2NHCO2Et, 55.8%, b16 137-7°, nD20 1.4480, d20 0.9653; 1-menthyl ester, 51.8%, b1 164.5°, nD20 1.4706, d20 0.9557, m. 45°; Et2NCH2CH2CH2NHCO2Et, 66.7%, b7 130°, nD20 1.4503; iso-Pr ester, 53.2%, b1.5 122-3°, nD30 1.4452, nD20 1.4493, d20 0.9367; sec-Bu ester, 42.5%, b5 132°, nD20 1.4513, d20 0.9334; C8H17 ester, 63.3%, b2 181.5-2°, nD30 1.4528, nD20 1.4577, d20 0.9168; cyclohexyl ester, 46.5%, b1.5 165-7°, nD30 1.4725, nD20 1.4752, d20 0.9765; 2-methylcyclohexyl ester, 81.5%, b2 177°, nD30 1.4693, nD20 1.4723, d20 0.9679; 1-menthyl ester, 88.2%, b3 173°, nD20 1.4719, d20 0.9482, m. 31°; Ph ester, 33.6%, b3 196-201°, nD20 1.4770; PhCH2 ester, 24%, b3 132-5°, nD20 1.5030. C5H5NCH2CH2CH2NHCO2Et, 78.3%, b9 150-3°, nD20 1.4742, d20 1.0070; Pr ester, 70.4%, b18 187-8°, nD20 1.4735, d20 0.9935; iso-Pr ester, 62.8%, b8 155-8°, nD20 1.4706, d20 0.9878; Bu ester, 62.8%, b3 146°, b5 167-8°, nD20 1.4730, d20 0.9788; iso-Bu ester, 53.5%, b2 136.5-7°, nD20 1.4710, d20 0.9813; iso-Am ester, 66.2%, b2 159.5°, nD20 1.4712, d20 0.9749; C8H17 ester, 63.7%, b9 212-13°, nD20 1.4720, d20 0.9550.

CC 10 (Organic Chemistry)

IT Nitriles  
(amino)

IT Amines  
(preparation of)

IT Ammonium, (2-cyanoethyl)dimethylpropyl-, bromide  
Ammonium, allyl(2-cyanoethyl)dimethyl-, chloride  
Dipropylamine, 3,3'-bis(diethylamino)-, picrate  
Piperidinium compounds, 1-(2-cyanoethyl)-1-ethyl-, iodide  
Piperidinium compounds, 1-(2-cyanoethyl)-1-methyl-, iodide

IT Carbamic acid, (3-piperidinopropyl)-  
(esters)

IT Ammonium, (2-cyanoethyl)ethyldimethyl-  
(halides)

IT 148-87-8, Propionitrile, 3-N-ethylanilino- 3217-00-3, Propionitrile,  
3,3'-(ethylenediimino)di- 22584-31-2, Propionitrile,  
3-(2-aminoethylamino)-  
(and derivs.)

IT 109-55-7, 1,3-Propanediamine, N,N-dimethyl- 1738-25-6, Propionitrile,  
3-dimethylamino- 5351-04-2, Propionitrile, 3-diethylamino- 6711-48-4,  
Dipropylamine, 3,3'-bis(dimethylamino)-  
(and salts)

IT 92-87-5, Benzidine 100-01-6, Aniline, p-nitro- 121-57-3, Sulfanilic  
acid  
(azo dyes from)

IT 82-71-3, Styphnic acid  
(compds. with amines)

IT 78-92-2, sec-Butyl alcohol 108-93-0, Cyclohexanol 111-87-5, Octyl  
alcohol 123-51-3, Isopentyl alcohol 463-73-0, Formic acid, chloro-  
583-59-5, Cyclohexanol, 2-methyl- 1490-04-6, Menthhol 188309-01-5,  
Carbamic acid, (3-dimethylaminopropyl)- 679426-41-6, Carbamic acid,  
(3-diethylaminopropyl)-  
(esters)

IT 107-13-1, Acrylonitrile

(in preparation of amino nitriles and polyamines)

IT 104-78-9, 1,3-Propanediamine, N,N-diethyl- 111-94-4, Propionitrile, 3,3'-iminodi- 151-18-8, Propionitrile, 3-amino- 3088-41-3, 1-Piperidinepropionitrile 3232-12-0, Benzamide, N,N-bis(2-cyanoethyl)- 3529-08-6, Piperidine, 1-(3-aminopropyl)- 6050-28-8, Dipropylamine, 3,3'-bis(diethylamino)- 6972-41-4,  $\beta$ -Alanine, N,N-diethyl- 7505-16-0, 1,3-Propanediamine, N,N-diethyl-, picrate 10517-44-9, 1,3-Propanediamine, dihydrochloride 16688-98-5, Propionitrile, 3,3'-iminodi-, hydrochloride 42350-94-7, Ammonium, (2-cyanoethyl)trimethyl-, iodide 43151-55-9, Propionamide, 3-N-ethylanilino- 59837-08-0,  $\beta$ -Alanine, N-ethyl-N-phenyl-, hydrochloride 66999-80-2, Benzamide, N-(3-diethylaminopropyl)- 70709-64-7,  $\beta$ -Alanine, N,N-diethyl-, sodium salt 93115-66-3, Ammonium, (2-cyanoethyl)diethylmethyl-, iodide 93507-56-3, Ammonium, (2-cyanoethyl)triethyl-, iodide

(preparation of)

IT 107-13-1, Acrylonitrile

(in preparation of amino nitriles and polyamines)

RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 37 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1952:23416 HCAPLUS

DN 46:23416

OREF 46:3976h-i,3977a-i,3978a

TI o-Quinones. II. The course of rearrangement of diazo ketones, o-quinonediazides, and acid azides

AU Horner, Leopold; Spietschka, E.; Gross, A.

CS Univ. Frankfurt a. M. Ger.

SO Ann. (1951), 573, 17-30

DT Journal

LA Unavailable

OS CASREACT 46:23416

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 45, 4217e. The probable mechanism of rearrangement (and decomposition) of compds. of type  $\text{R.C}(\text{:O})\text{C}(\text{:N}_2)\text{R}'$  under the influence of ultraviolet light is outlined. The source of light was a "Labortauch" lamp S81 which was jacketed and could be cooled to  $0^\circ$  (or below). Ordinarily pure N was bubbled through (170 cc. of) the irradiated solution at low temps.  $\text{BzC}(\text{:N}_2)\text{Ph}$  (I) (4.4 g.) irradiated in  $\text{Et}_2\text{O}$  gave 3.5 g.  $\text{Ph}_2\text{C:C:O}$  (identified as  $\text{Ph}_2\text{CHCONHPh}$ , m.  $180^\circ$ ). I (4.4 g.) irradiated in 165 cc. dioxane and 5 cc.  $\text{H}_2\text{O}$  gave a good yield of  $\text{Ph}_2\text{CHCO}_2\text{H}$ , m.  $145^\circ$ , and in  $\text{EtOH}$  gave  $\text{Ph}_2\text{CHCO}_2\text{Et}$ , m.  $57^\circ$ .  $\text{BzCH:N}_2$  (II) irradiated in  $\text{Et}_2\text{O}$  gave a polymer  $(\text{C}_8\text{H}_6\text{O})_x$  not melting at  $260^\circ$ , almost insol. in organic solvents, giving a red solution in  $\text{H}_2\text{SO}_4$ . Irradiated in aqueous dioxane, II gave  $\text{PhCH}_2\text{CO}_2\text{H}$ , m.  $76^\circ$ , and, in absolute alc.,  $\text{PhCH}_2\text{CO}_2\text{Et}$ . When the irradiation was carried out in dioxane and  $\text{PhNH}_2$ ,  $\text{PhCH}_2\text{CONHPh}$ , m.  $116^\circ$ , was formed. Irradiated with  $\text{PhN:NPh}$  (III) in  $\text{C}_6\text{H}_6$ , II gave  $\text{PhCH.CO.NPh.NPh}$ , m.  $92^\circ$ ; similarly I and III in  $\text{Et}_2\text{O}$  gave  $\text{Ph}_2\text{C.CO.NPh.NPh}$ , m.  $173^\circ$  (cf. Cook and Jones, C.A. 35, 4765.1). 1,2- $\text{C}_6\text{H}_4.\text{CO.C}(\text{:N}_2).\text{CH:CH}$  (IV) in absolute alc. containing traces of  $\text{HCl}$  gas, when irradiated (under anhydrous conditions) until the coupling reaction with naphthol had ceased, gave 1,2- $\text{C}_6\text{H}_4.\text{CH}(\text{CO}_2\text{Et}).\text{CH:CH}$ , b16  $160^\circ$ ; corresponding anilide,  $\text{C}_{16}\text{H}_{13}\text{ON-}$ , leaflets, m.  $162^\circ$  (from  $\text{C}_6\text{H}_6$ ) (cf. Sus, C.A. 40, 5420.5, 5422.7).  $\text{BzN}_3$  irradiated in 100

cc. of an unidentified solvent at 6° gave about 87% PhNCO [identified by conversion into (PhNH)2CO, m. 232.5° (from alc.), the mother liquors from which gave BzNHPh, m. 165°]. To 50 cc. dry boiling xylene were added dropwise 10 g. IV in 100 cc. xylene, giving 6-7 g. of the dimeric indene ketene (V), m. 256° (from CHCl3 or AcOEt), and not the dinaphthalene dioxide structure ascribed to this product by Bamberger, et al. (C.A. 17, 2577). Hydrogenation in AcOEt with Raney Ni yielded the corresponding indan ketene, C20H16O2, yellow, m. 200-201°. V (5 g.) dissolved in 100 cc. hot glacial AcOH gave the compound (VI), colorless, m. 182-3°, giving a red enol reaction with FeCl3, a deep blue color with alkali, coupling with diazonium compds., and on hydrogenation adding 2 H2 to give the indan derivative, C20H18O3, m. 110° (decomposition) (from C6H6-petr. ether), whose Me ester (VII), viscous yellow oil, b5 220°. N2H4.H2O refluxed with VII in EtOH gave the monomeric hydrazide, C10H12ON2, m. 128°. Similarly HONH2 and VII yielded 1-indanhydroxamic acid, C10H11O2N, m. 170° (decomposition). ClC:CCl.CCl:CCl.CO.CO (VIII) (0.06 mole) and 0.02 mole I in 170 cc. Et2O were irradiated 1 hr., another 0.06 mole VIII then added, and finally another portion of VIII; the total irradiation period was 4 hrs. The product was the compound (IX), prisms, m. 187-8° (from CCl4). IX was also obtained, together with small amts. of tetrachloropyrocatechol, in 80% yield by refluxing VIII with Ph2C:CO in Et2O. Similarly prepared was the tetra-Br analog of IX, m. 218°. Heating (4.4 g.) IX 15 min. with 2 N aqueous NaOH and allowing to stand overnight gave 0.02 g. of an unidentified red compound, the filtrate from which, on acidification and Et2O extraction, yielded 1 g. of another unidentified substance. The Et2O extract on treatment with N2CH2 gave 2.2 g. tetrachloroveratrole, m. 88°, and from the mother liquors after refluxing with (solid) KOH, followed by addition of H2O, filtration, and acidification, was obtained 50 mg. Ph2C(OH)CO2H (m.p. not given). Me2CBrCOBr (under CO2) in Et2O was treated gradually with Zn turnings yielding Me2C:CO, which was distilled directly into VIII in Et2O and the mixture refluxed yielded the di-Me analog (X) of IX, C10H6O3Cl4, m. 148-9° (from Et2O), recovered unchanged from an alkaline solution by acidification. Practically no polymerization occurred when 20 cc. CH2:CHCN in C6H6 was mixed with I, II, or IV, followed by ultraviolet irradiation, and only traces of polyacrylonitrile (< 1%) were formed when CH2:CHCN was irradiated in C6H6 and BzN3 or in C6H6 (in a CO2 atmospheric) and PhN3.

CC 10 (Organic Chemistry)

IT Ketones

(diazo, rearrangement by ultraviolet light)

IT Rearrangements

(of diazo ketones, o-quinone diazides and acid azides)

IT Azides

(rearrangement of, by ultraviolet light)

IT Light, uv

(rearrangements of diazo ketones, quinone diazides and acid azides in)

IT Quinones

(o-)

IT 1-Indeneacetanilide

Indan ketene, dimer

Inden ketene, dimer

IT Quinone diazides

(rearrangement of ortho, by ultraviolet light)

IT 103-71-9, Isocyanic acid, phenyl ester

(from BzN3)

IT 582-61-6, Benzoyl azide 879-15-2, 1(2H)-Naphthalenone, 2-diazo-

(irradiation with ultraviolet light)

IT 76-93-7, Benzoic acid 101-97-3, Acetic acid, phenyl-, ethyl ester

103-82-2, Acetic acid, phenyl- 117-34-0, Acetic acid, diphenyl-  
 525-06-4, Ketene, diphenyl- 621-06-7, Acetanilide, 2-phenyl- 944-61-6,  
 Veratrole, 3,4,5,6-tetrachloro- 3468-99-3, Acetic acid, diphenyl-, ethyl  
 ester 4695-14-1, Acetanilide, 2,2-diphenyl- 14383-98-3,  
 1,2-Diazetid-3-one, 1,2,4-triphenyl- 60585-46-8, Dispiro[indene-1,1'-  
 cyclobutane-3',1''-indene]-2',4'-dione 99067-94-4, 1-Indancarboxylic  
 acid, hydrazide 101611-77-2, 1,2-Diazetid-3-one, tetraphenyl-  
 170856-46-9, 1-Indeneacetic acid, ethyl ester 411210-42-9, Acetic acid,  
 diphenyl(2,3,4,5-tetrachloro-6-hydroxyphenoxy)-,  $\delta$ -lactone  
 854877-16-0, Dispiro[indan-1,1'-cyclobutane-3',1''-indan]-2',4'-dione  
 856810-42-9, Propionic acid, 2-methyl-2-(2,3,4,5-tetrachloro-6-  
 hydroxyphenoxy)-,  $\delta$ -lactone 857556-71-9, Acetic acid,  
 diphenyl(2,3,4,5-tetrabromo-6-hydroxyphenoxy)-,  $\delta$ -lactone  
 858225-56-6, 1-Indancarbohydroxamic acid 858225-96-4, 1-Indancarboxylic  
 acid, 1-(1-indanylcabonyl)- 858226-50-3, 1-Indancarboxylic acid,  
 1-(1-indanylcabonyl)-, methyl ester 860358-30-1, 1-Indenecarboxylic  
 acid, 1-(1-indenylcabonyl)-  
 (preparation of)  
 IT 107-13-1, Acrylonitrile  
 (reaction with diazo ketones and azides with ultraviolet irradiation)  
 IT 598-26-5, Ketene, dimethyl-  
 (reaction with tetrachloro-o-benzoquinone in ultraviolet light)  
 IT 2435-53-2, o-Benzoquinone, tetrachloro-  
 (reactions of, in ultraviolet light)  
 IT 622-37-7, Benzene, azido-  
 (reactions of, with acrylonitrile with ultraviolet irradiation)  
 IT 334-88-3, Methane, diazo-  
 (reactions of, with o-quinones)  
 IT 3469-17-8, Acetophenone, 2-diazo-2-phenyl-  
 (rearrangement by ultraviolet light)  
 IT 3282-32-4, Acetophenone, 2-diazo-  
 (rearrangement of, by ultraviolet light)  
 IT 107-13-1, Acrylonitrile  
 (reaction with diazo ketones and azides with ultraviolet irradiation)  
 RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 38 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1951:11211 HCAPLUS

DN 45:11211

OREF 45:2005c-i

TI Meyer's synthesis of pyridines from acrylonitriles. Verification in the  
 light of Gastaldi's objections

AU Palit, Nirmalananda

CS Science Coll., Patna

SO J. Indian Chem. Soc. (1950), 27, 71-6

DT Journal

LA Unavailable

AB It is shown that the C<sub>6</sub>H<sub>6</sub>N structures assigned by Meyer (C.A. 3, 1747) are  
 correct in general. An exception, 2,4-diphenyl-6-methylpyridine (I),  
 noted by Gastaldi (C.A. 16, 2515, 2689), is probably confirmed.  
 PhC(NH<sub>2</sub>):CHCN (2.8 g.), 5 g. PhC(OEt):CHBz, and absolute alc. added to alc.  
 NaOEt (0.46 g. Na) and left 1 day give 2 g. 3-cyano-2,4,6-  
 triphenylpyridine (II), m. 220° (from alc.) as reported by M. and  
 I. II and fuming HCl, heated 4 h. in a sealed tube at 260° and

diluted with H<sub>2</sub>O, give 2,4,6-triphenylpyridine, m. 136-7°.  
 m-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OH (2.5 g.), 5 g. PhCH:CHBz (III), and 40 mL. absolute alc. refluxed 7 h. with addition of a few drops alc. KOH, give 3 g. 7-hydroxy-2,4-diphenylquinoline (IV), m. 273° (from C<sub>6</sub>H<sub>6</sub>). To 3 g. IV in 450 mL. aqueous KOH (3 g. excess) on a H<sub>2</sub>O bath is added slowly (stirring) 9 g. tech. KMnO<sub>4</sub> as a 5% solution, the excess KMnO<sub>4</sub> decomposed with SO<sub>2</sub>, and the mixture filtered hot; by a tedious isolation and purification process, a poor yield of 2,4-diphenyl-5,6-pyridinedicarboxylic acid, m. 185° (from absolute alc.), is obtained. To 20 g. III, 14 g. CNCH<sub>2</sub>CO<sub>2</sub>Et (V), and 30 g. MeOH is added 5% MeOHNaOMe (VI) to alkalinity (all chems. must be very dry and pure), the mixture refluxed 2 h. with frequent 2-drop addns. of VI to keep alkaline, and left overnight; solvent removal, Et<sub>2</sub>O extraction of the residue, and Na<sub>2</sub>CO<sub>3</sub> washing, drying, and evaporation of the Et<sub>2</sub>O give, on distillation, a few drops V, then 28 g. of a viscous mass (VII), b<sub>10</sub> 100-200°. VII in warm CCl<sub>4</sub>, saturated with dry HBr, left at 0°, and the mass rubbed with MeOH, gives 22 g. Et 2-keto-4,6-diphenyltetrahydro-3-pyridinecarboxylate (VIII), m. 160° (from alc.). Hydrolysis of VIII gives the acid. VII in hot AcOH is treated with Br, and the NH<sub>4</sub>Br filtered off; evaporation in vacuo leaves a residue which, dried over KOH, boiled with H<sub>2</sub>O, treated with hot aqueous NaOH (IX), and recrystd. repeatedly from alc. (Norit and kieselguhr), gives a low yield of Et 2-bromo-4,6-diphenyl-3-pyridinecarboxylate (X), m. 133-5°. IX gives some VIII. X (5 g.), 1 g. red P, and 12 mL. HI (d. 1.94) heated in a sealed tube 24 h. at 175-80° give crystals which, treated with boiling KOH and the solution concentrated and acidified, give an acid; this is refluxed 2 h. with powdered Ba(OH)<sub>2</sub> and a little H<sub>2</sub>O, and the dried material (1 g.) gently heated (free flame) with Ba(OH)<sub>2</sub>, giving 0.5 g. distillate of 2,4-diphenylpyridine (XI), m. 68° (picrate, m. 189°) (cf. Gastaldi, loc. cit.). XI (1 g.) and 1.5 g. MeI refluxed 1 h. give the methiodide (XII), m. 206-8° (from alc.). XII (4 g.) is heated 2 h. in a sealed tube at 300-15°, dissolved in hot H<sub>2</sub>O, treated with concentrated NaOH, and steam-distilled; the Et<sub>2</sub>O-soluble portion of the residue gives, from ligroin, mainly XI (identified as the picrate). The ligroin filtrate gives, on evaporation, a few crystals of presumably I, m. 69-72° (from C<sub>6</sub>H<sub>6</sub>-ligroin); picrate, m. 212°, in agreement with G., loc. cit.

- CC 10 (Organic Chemistry)  
 IT Ring closure or formation  
     (pyridine derivs. by)  
 IT 110-86-1, Pyridine  
     (derivs., from acrylonitriles)  
 IT 107-13-1, Acrylonitrile  
     (derivs., pyridines from)  
 IT 580-35-8, Pyridine, 2,4,6-triphenyl- 1912-16-9, 2-Picoline,  
     4,6-diphenyl- 26274-35-1, Pyridine, 2,4-diphenyl- 26274-36-2,  
     Pyridine, 2,4-diphenyl-, picrate 55249-89-3, Nicotinonitrile,  
     2,4,6-triphenyl- 107931-55-5, 7-Quinolinol, 2,4-diphenyl- 113926-73-1,  
     2-Picoline, 4,6-diphenyl-, picrate 846049-38-5, Nicotinic acid,  
     2-bromo-4,6-diphenyl-, ethyl ester 856963-09-2, Pyridinium,  
     1-methyl-2,4-diphenyl-, iodide 858474-69-8, Quinolinic acid,  
     4,6-diphenyl- 860233-48-3, 7-Quinolinol, 2,4-diphenyl-, picrate  
     860403-48-1, Nicotinic acid, tetrahydro-2-oxo-4,6-diphenyl-, ethyl ester  
     (preparation of)  
 IT 107-13-1, Acrylonitrile  
     (derivs., pyridines from)  
 RN 107-13-1 HCAPLUS  
 CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 39 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1949:36515 HCAPLUS

DN 43:36515

OREF 43:6578e-i,6579a-f

TI Decarboxylation and cyclization reactions of some pimelic acid derivatives

AU Frank, Robert L.; McPherson, James B., Jr.

SO Journal of the American Chemical Society (1949), 71, 1387-91

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA Unavailable

OS CASREACT 43:36515

AB MeC(:CH<sub>2</sub>)CAc(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>2</sub> (I), prepared in 35% yield from 98 g. pure mesityl oxide (II), 106 g. CH<sub>2</sub>:CHCN, 79 g. Me<sub>3</sub>COH, and 5 g. Triton B, m. 115-17° (cf. Bruson and Riener, C.A. 37, 1381.7). The purity of II was critical, com. II giving low yields. Saponification of 28.6 g. I with 20.8 g. KOH and 230 ml. H<sub>2</sub>O according to B. and R. gave 72% acid analog (III) of I, m. 137.5-8.5°; the haloform reaction with III in 20% NaOH with 9.5% NaOCl gave 67% MeC(:CH<sub>2</sub>)C(CO<sub>2</sub>H)(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub> (IV), m. 158-60°. Rearrangement of the propenyl group in IV: 46.7 g. IV and 1.51 g. BaCO<sub>3</sub> intimately mixed and heated (3 batches, thermometer bulb in bottom of **distilling** flask) gave much **gas** at 285°, a temperature drop to 275°, and a rise to 320° with **distn** of H<sub>2</sub>O and yellow oil, **extracted** with Et<sub>2</sub>O to give 12 g. 4-isopropylidenecyclohexanone (V), b<sub>1</sub> 54°, n<sub>D</sub>20 1.4817, d<sub>20</sub>20 0.959, MR calculated 41.1, MR found 41.2, cedarlike odor; semicarbazone, m. 196-8° (6 crystns. from EtOH); 2,4-dinitrophenylhydrazone, m. 130.5-2° (3 crystns. from MeOH and 7 from MeOH). Addition of 1320 cc. 4% O<sub>3</sub> during 2.5 hrs. to 1.01 g. V in 15 cc. CH<sub>2</sub>Cl<sub>2</sub> in a Dry-Ice bath, then dropwise addition at room temperature to 1.7 g. 30% H<sub>2</sub>O<sub>2</sub>, 0.1 cc. H<sub>2</sub>SO<sub>4</sub>, and 35 cc. H<sub>2</sub>O, keeping 45 min. at room temperature, refluxing 1 hr. (CH<sub>2</sub>Cl<sub>2</sub> vapor contained no CH<sub>2</sub>O), then **distilling**, gave 24 cc. H<sub>2</sub>O containing a trace of CH<sub>2</sub>O and HCO<sub>2</sub>H, and giving a strong test for Me<sub>2</sub>CO (CHI<sub>3</sub> and 2,4-dinitrophenylhydrazone). The **alkaline distillation** residue was **extracted** with Et<sub>2</sub>O, acidified, and saturated with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, precipitating a brown oil. CHCl<sub>3</sub> **extraction** of the filtrate, concentration, and crystallization from 95% EtOH gave 1,4-cyclohexanedione, m. and mixed

m. p. 77-8°. V (3.98 g.) in Et<sub>2</sub>O added slowly to MeMgI (from 15.6 g. MeI and 2.64 g. Mg) in anhydrous Et<sub>2</sub>O, then left 16 hrs. and added to 8 g. NH<sub>4</sub>Cl in ice and 125 g. H<sub>2</sub>O, HCl added to pH 6, and steam **distillation** of the Et<sub>2</sub>O **extract** gave 0.77 g. oil, b<sub>1</sub> 65°, crystallized on chilling to γ-terpineol, m. 63-7° (sublimed at 45-50° and 15 mm.), lilac odor. Confirmation of the possible decarboxylation of IV before cyclization to V was shown by heating 5 g. IV with 0.5 g. Cu-bronze powder to 195-205°, with formation of CO<sub>2</sub> and 39% Me<sub>2</sub>C:C(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub> (Va), m. 104.5-6°. Dropwise addition of 0.596 mole I in 810 cc. dioxane (peroxide-free) to 2.68 moles NaOCl in 2300 cc. H<sub>2</sub>O and 850 cc. dioxane at 0-10°, addition after 4 hrs. at 0-10° of **aqueous** NaHSO<sub>3</sub>, washing with Et<sub>2</sub>O, acidification with concentrated HCl, filtration of the precipitate after 12 hrs., precipitation from 900 cc. hot H<sub>2</sub>O by chilling, and crystallization from CH<sub>2</sub>Cl<sub>2</sub> gave 81% MeC(:CH<sub>2</sub>)C(CO<sub>2</sub>H)(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>2</sub> (VI), m. 166-7.5°. VI (45 g.), 4.5 g. Cu-bronze, and 4.5 g. powdered soft glass were heated under N to 200-30° with CO<sub>2</sub> evolution, then cooled, the C<sub>6</sub>H<sub>6</sub> **extract** washed with dilute H<sub>2</sub>SO<sub>4</sub> and NaHCO<sub>3</sub>, Et<sub>2</sub>O added, and the filtrate

distilled to give 12.3 g.  $\text{Me}_2\text{C}:\text{C}(\text{CH}_2\text{CH}_2\text{CN})_2$  (VII), b1 135-7°, nD<sub>20</sub> 1.4733. The residue above, insol. in  $\text{C}_6\text{H}_6$  and Et<sub>2</sub>O, was extd . with  $\text{Me}_2\text{CO}$ , the filtrate concentrated, and the solid crystallized from dilute HCl and EtOH to give 26%  $\alpha$ -(2-cyanoethyl)- $\alpha$ -isopropenylglutarimide (VIII), m. 119-21°, soluble in 5% NaOH, insol. in 5%  $\text{NaHCO}_3$ ; heating with Cu bronze to 350° gave no  $\text{CO}_2$ , only a black tar. VII in boiling 2 N NaOH 6 hrs. gave Va. VII 2 g. in 25 cc. pure  $\text{CCl}_4$  at 0° was treated with 12 l. of 2.6%  $\text{O}_3$  during 1 hr., the solvent evaporated at 30° and 30 mm., 70 g.  $\text{H}_2\text{O}$  and 2.85 g. Zn added, and 50 cc. distilled into 10 cc.  $\text{H}_2\text{O}$  at 0°, giving no  $\text{CH}_2\text{O}$  or  $\text{HCO}_2\text{H}$ , but 17%  $\text{Me}_2\text{CO}$  (2,4-dinitrophenylhydrazone). VIII heated just below the b. p. with N KOH 1 hr., the acidified solution concentrated to dryness, and crystallization from  $\text{Me}_2\text{CO}$  gave 77%  $\text{MeC}(:\text{CH}_2)\text{C}(\text{CONH}_2)(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m. 164.5-6 °; boiling 3% aqueous KOH 16 hrs. or boiling  $\text{H}_2\text{SO}_4$ - $\text{HNO}_2$  mixture (Cf. Haller and Bauer, C.A. 5, 3411) 1 hr. gave no hydrolysis. Dropwise addition of 16.3 g. VII in Et<sub>2</sub>O to gently refluxing  $\text{PhNHtLi}$  [prepared from 47.6 g.  $\text{PhNHt}$  according to Ziegler, (C.A. 29, 746.4)] in Et<sub>2</sub>O during 5 hrs., addition to 360 cc. 2 N HCl, and Et<sub>2</sub>O extraction gave 13.8 g. crude 2-cyano derivative of V; 10% NaOH and 37 and 50%  $\text{H}_2\text{SO}_4$  were without effect but refluxing with 10%  $\text{H}_2\text{SO}_4$ , steam distillation, 12 hrs.' more refluxing, and steam distillation gave hydrolysis and decarboxylation, V being isolated in low yield by Et<sub>2</sub>O extraction and identified as the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 130-2° (from EtOH); semicarbazone, m. 193-5°, mixture with authentic derivative (m. 196-8°) m. 176-85°. The formation of the isomeric semicarbazone may indicate the presence of the isopropenyl analog of V. Infrared spectra did not differentiate between the  $\text{Me}_2\text{C}$  and the  $\text{MeC}(:\text{CH}_2)$  groups, both types of compds. showing maximum between 890 and 918  $\text{cm}^{-1}$ .

- CC 10 (Organic Chemistry)
- IT Rearrangements
  - (of isopropenyl group)
- IT Cyanoethylation
  - (of mesityl oxide)
- IT Ring closure or formation
  - (of pimelic acid derivs.)
- IT Spectra
  - (of  $\gamma$ -acetyl- $\gamma$ -isopropenylpimelic acid and  $\alpha$ -(2-cyanoethyl)- $\alpha$ -isopropenyl-glutarimide)
- IT Isopropenyl group
  - (rearrangement of)
- IT Carboxyl group
  - (removal of, from pimelic acid derivs.)
- IT 16400-79-6, Heptanedinitrile, 4-acetyl-4-isopropenyl- 19620-36-1, Cyclohexanone, 4-isopropylidene- (and derivs.)
- IT 141-79-7, Mesityl oxide (cyanoethylation of)
- IT 111-16-0, Pimelic acid (derivs.)
- IT 586-81-2,  $\gamma$ -Terpineol 4379-08-2, 1,3,5-Pentanetricarboxylic acid, 3-isopropenyl- 26430-98-8, Heptanedioic acid, 4-isopropylidene- 412036-11-4, Heptanedioic acid, 4-acetyl-4-isopropenyl- 500302-78-3, Butyric acid, 4-cyano-2-(2-cyanoethyl)-2-isopropenyl- 500302-78-3, 3-Butenoic acid, 2,2-bis(2-cyanoethyl)-3-methyl- 688302-50-3, Aconitic acid,  $\alpha$ -hydroxy- 854704-91-9, Glutarimide, 2-(2-cyanoethyl)-2-isopropenyl- 855895-60-2, Heptanedinitrile, 4-isopropylidene- 855896-79-6, Heptanedioic acid, 4-carbamoyl-4-isopropenyl- (preparation of)
- IT 107-13-1, Acrylonitrile

(reaction with mesityl oxide)  
IT 107-13-1, Acrylonitrile  
(reaction with mesityl oxide)  
RN 107-13-1 HCAPLUS  
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 40 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1946:29318 HCAPLUS

DN 40:29318

OREF 40:5733h-i,5734a-h

TI Synthesis of monoalkyl-substituted diamines and their condensation products with 4,7-dichloroquinoline

AU Pearson, D. E.; Jones, W. H.; Cope, Arthur C.

CS Mass. Inst. Technol., Cambridge

SO Journal of the American Chemical Society (1946), 68, 1225-9

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA Unavailable

AB Cyclohexanone (I) (25 g.) and 30 g. anhydrous  $\text{C}_2\text{H}_4(\text{NH}_2)_2$ , allowed to stand 1 h. and the mixture hydrogenated in 25 mL. absolute EtOH with Pt oxide at room temperature and an initial H pressure of 2 atmospheric for 12 h., give 83% of N-cyclohexylethylenediamine, b4 101-2°, nD25 1.4800, d425 0.9153 (all n and d. at 25°).  $\text{Me}_2\text{CO}$  (116 g.), slowly added to cooled  $\text{C}_2\text{H}_4(\text{NH}_2)_2$ , the mixture allowed to stand overnight, and hydrogenated in 50 mL. absolute EtOH at 60° with 2 g. Pt oxide for 12 h., gives 50% of N-isopropylethylenediamine, b767 135.5-7.5°, n 1.4350, d. 0.8232. I (49 g.) and 90 g.  $(\text{H}_2\text{NCH}_2)_2\text{CHOH}$ , mixed with cooling and the mixture reduced in 50 mL. absolute EtOH at 60° over Pt oxide (90% complete in 5 h., complete in 16 h.), give 77% of 1-cyclohexylamino-3-amino-2-propanol, b2 126-8°, m. 29-32°, n 1.4997, d. 1.0135; reduction in EtOH over Raney Ni at 160°/200 atmospheric for 12 h. gives 47%.  $\text{CH}_2:\text{CHCN}$  (106.1 g.), added dropwise to 177.3 g. iso-PrNH<sub>2</sub> at a temperature below 30° and the mixture stirred overnight at room temperature, give 95% of β-isopropylaminopropionitrile, b17 86-7°, n 1.4290, d. 0.8641; reduction of 190 g. over 20 g. Raney Ni at 100°/120 atmospheric gives 54% of N-isopropyltrimethylenediamine, b770 161-2°, n 1.4394, d. 0.8271. Iso-PrNH<sub>2</sub> (45 g.) and 26.5 g.  $\text{Na}_2\text{CO}_3$  in 300 mL.  $\text{H}_2\text{O}$  and 50 mL. EtOH at 20-30°, treated dropwise with 60 g.  $\text{Ac}(\text{CH}_2)_3\text{Cl}$  (II), the mixture allowed to stand overnight, added rapidly to a mixture of 53 g.  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and 30 cc. NaOH in 100 mL.  $\text{H}_2\text{O}$  at 20-5°, allowed to stand overnight, and extracted with ether for 12 h., give 50% of 5-isopropylamino-2-pentanone oxime (III), pale yellow, b0.5 92-7°, m. 80.5-1.5°; iso-BuNH<sub>2</sub> similarly gives 34% of the iso-Bu homolog (IV), m. 45-6°; tert-BuNH<sub>2</sub> (20 g.) and 37.3 g. anhydrous  $\text{K}_2\text{CO}_3$  at 50-60°, treated dropwise (1 h.) with 32.6 g. of II, 75 mL.  $\text{C}_6\text{H}_6$  added, the bath heated to 90-5° during 4 h. and maintained at that temperature for 20 h., the  $\text{C}_6\text{H}_6$  solution washed with 3 100-mL. portions of 3 N HCl, the acid exts. made alkaline with  $\text{K}_2\text{CO}_3$  and reacted with  $\text{NH}_2\text{OH}$ , give 11% of the tert-Bu homolog (V), m. 134-4.5°. III (0.1 mol) in 250 mL. BuOH, reduced with 23 g. Na (refluxing until all the Na is dissolved), gives 58% of 1-isopropylamino-4-aminopentane, b3 55-6°, n 1.4400, d. 0.8166; IV gives 61% of the iso-Bu homolog, b1 60-1°, n 1.4411, d. 0.8198; V yields 53% of the tert-Bu homolog, b13 84-7°, n 1.4398, d. 0.8178. 4,7-Dichloroquinoline (VI) (0.205 mol) and 0.20 mol of the diamine were heated at between 120-30° for 1-2



h. and then at 130-5° for an addnl. 2 h., giving 7-chloro-4-monoalkylaminoalkylaminoquinolines. VI (40.6 g.) and 12 g. C<sub>2</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> in 40 g. PhOH, heated 4 h. at 110-20°, the cooled product extracted with ether, the solid HCl salts added to 50 g. KOH in 300 mL. H<sub>2</sub>O and 400 mL. EtOH and shaken overnight, give 20 g. of 4,4'-(ethylenediimino)bis(7-chloroquinoline) (SN 14,725); crystallized from 800 mL. [CH<sub>2</sub>(OH)CH<sub>2</sub>]<sub>2</sub>O, the yield is 37%, m. 334.5-7° (decomposition); the alkaline filtrate yields 9 g. (21%) of 4-(2-aminoethylamino)-7-chloroquinoline (SN 14,724), m. 137-9°. 4-(Isopropylaminoethylamino) analog (SN 14,155), m. 129-30°, 52%; 4-(2-cyclohexylaminoethylamino) analog (SN 14,156), m. 151-1.5°, 48%; 4-(3-cyclohexylamino-2-hydroxypropylamino) analog (SN 14,689), m. 145.5-6°, 37%. 4-(3-Isopropylaminopropylamino) analog (SN 14,846), m. 107.5-8°, 51%. (H<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>CHOH (17.1 g.) and 39.6 g. VI with 20 g. PhOH, heated at 120-30° for 1 h., when the temperature of the reaction mixture suddenly rises to 175°, give 36% of 1,3-bis(7-chloro-4-quinolylamino)-2-propanol (SN 14,865), m. 143-5° and then 261-3° (decomposition); the 1:1 condensation product was not isolated. The 1-alkylamino-4-aminopentanes were added to about 25% of their weight of PhOH and a 2-3% mol. excess of VI and heated 4 h. at 150-60°; the products distilled at bath temps. of 180-200° as viscous yellow oils which solidified on standing. 4-(4-Isopropylamino-1-methylbutylamino)-7-chloroquinoline (SN 14,079), m. 103-5.5°, 48%; 4-(4-isobutylamino-1-methylbutylamino) homolog (SN 15,067), m. 72-4°, 28%; 4-(4-tert-butylamino-1-methylbutylamino) homolog, m. 117-17.5°, 49%.

CC 10 (Organic Chemistry)

IT Amines

(alkyl-substituted di-, reactions of, with chloro quinolines)

IT Ketones

(reactions of, with ethylenediamine)

IT 692-98-8, Propionitrile, β-isopropylamino- 3360-16-5,  
 1,3-Propanediamine, N-isopropyl- 5407-57-8, Quinoline,  
 4-(2-aminoethylamino)-7-chloro- 5418-54-2, Quinoline,  
 7-chloro-4-(3-isopropylaminopropylamino)- 5427-42-9, Quinoline,  
 7-chloro-4-(2-cyclohexylaminoethylamino)- 5700-53-8, Ethylenediamine,  
 N-cyclohexyl- 6285-24-1, 2-Propanol, 1,3-bis(7-chloro-4-quinolylamino)-  
 19522-67-9, Ethylenediamine, N-isopropyl- 500533-57-3, Quinoline,  
 7-chloro-4-(2-isopropylaminoethylamino)- 500533-69-7, 2-Propanol,  
 1-(7-chloro-4-quinolylamino)-3-cyclohexylamino- 500533-69-7, Quinoline,  
 7-chloro-4-(3-cyclohexylamino-2-hydroxypropylamino)- 720685-07-4,  
 2-Pentanone, 5-tert-butylamino-, oxime 769951-95-3, Quinoline,  
 7-chloro-4-(4-isopropylamino-1-methylbutylamino)- 854901-22-7,  
 2-Propanol, 1-amino-3-cyclohexylamino- 855760-21-3, Quinoline,  
 4,4'-(ethylenediimino)bis[7-chloro- 858277-97-1, Quinoline,  
 4-(4-tert-butylamino-1-methylbutylamino)-7-chloro- 860544-42-9,  
 1,4-Pentanediamine, N1-isopropyl- 860544-44-1, 1,4-Pentanediamine,  
 N1-isobutyl- 860546-22-1, 2-Pentanone, 5-isopropylamino-, oxime  
 860546-24-3, 2-Pentanone, 5-isobutylamino-, oxime 861014-94-0,  
 1,4-Pentanediamine, N1-tert-butyl-

(preparation of)

IT 67-64-1, Acetone

(reaction of, with ethylenediamine)

IT 75-64-9, tert-Butylamine 78-81-9, Isobutylamine

(reaction with 5-chloro-2-pentanone)

IT 86-98-6, Quinoline, 4,7-dichloro- 5891-21-4, 2-Pentanone, 5-chloro-

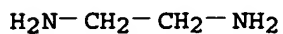
(reaction with amines)

IT 108-94-1, Cyclohexanone

(reaction with diamines)

IT 107-15-3, Ethylenediamine

(reaction with ketones)  
IT 75-31-0, Isopropylamine 616-29-5, 2-Propanol, 1,3-diamino-  
(reactions of)  
IT 107-13-1, Acrylonitrile  
(reactions of, with isopropylamine)  
IT 107-15-3, Ethylenediamine  
(reaction with ketones)  
RN 107-15-3 HCAPLUS  
CN 1,2-Ethanediamine (9CI) (CA INDEX NAME)



IT 107-13-1, Acrylonitrile  
(reactions of, with isopropylamine)  
RN 107-13-1 HCAPLUS  
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



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